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Supported palladium-platinum catalyst for methane combustion at high pressure

K. Persson[a,*], A. Ersson[a], A. Manrique Carrera[b], J. Jayasuriya[b], R. Fakhrai[b], T. Fransson[b], S. Järås[a]

[a]KTH, Department of Chemical Engineering and Technology/Chemical Technology, Teknikringen 42, SE-10044 Stockholm, Sweden
[b]KTH, Department of Energy Technology/Heat and Power Technology, SE-10044 Stockholm, Sweden

Abstract

Catalytic combustion of methane over a supported bimetallic Pd-Pt catalyst and a monometallic Pd catalyst has been investigated experimentally. Two different reactor configurations were used in the study, i.e. a tubular lab-scale reactor working at atmospheric pressure and a high-pressure reactor working at up to 15 bar. The results showed that the bimetallic catalyst has a clearly more stable activity during steady-state operation compare to the palladium only catalyst. The activity of the bimetallic catalyst was slightly higher than for the palladium catalyst. These results were established in both test facilities. Further, the impact of pressure on the combustion activity has been studied experimentally. The tests showed that the methane conversion decreases with increasing pressure. However, the impact of pressure is more prominent at lower pressures and levels out for pressures above 10 bar.

Keywords: High pressure; Palladium; Platinum; Bimetallic catalysts; Methane; Combustion stability

1. Introduction

Catalytic combustion has received considerable attention lately due to its ability to reduce the emission of NO_x from gas turbines down to ultra low levels [1,2]. In a conventional gas turbine combustor, the temperature is increased from the compressor outlet temperature of 350–500 °C up to 1500 °C. Since turbines cannot stand this high outlet temperature from the combustor, cooling of the gas mixture is necessary with by-passed air. This cooling step is not needed for a catalytic combustor since its outlet temperature does not exceed 1300 °C. Even so, there is no single catalyst material available that is able to work in the entire temperature range for a catalytic combustor. For that reason, catalytic combustors are often divided into at least two segments, i.e. an ignition catalyst and a more thermally resistant catalyst. The ignition catalyst is the first segment in a catalytic combustor. Its task is to raise the temperature of the compressor outlet gas to temperatures where the more thermally resistant catalysts ignites. If the ignition catalyst has insufficient activity to ignite at the required temperature, pre-heaters are necessary. Pre-heaters cause an increase of fuel consumption, as well as elevated emission of NO_x. Hence, it is important to have a very active ignition catalyst in order to avoid pre-heaters.

Supported palladium catalysts are widely known as excellent catalysts for methane combustion and are therefore often used as ignition catalysts [1,3]. However, it has recently been shown that the palladium catalysts have difficulty to maintain their high activity during longer periods of steady state operation [4,5]. Since palladium-based catalysts have such a high initial activity, it is desirable to stabilise this activity. An effective method for improving the stability is to incorporate a co-metal such as platinum into the palladium catalyst [4–9].

Most activity tests published on ignition catalysts have been performed at atmospheric pressure and relatively low gas velocities, <2 m/s. Since a gas turbine works at pressures of up to 30 bar and gas velocities >10 m/s,

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[*] Corresponding author. Tel.: +46 8 790 82 81; fax: +46 8 10 85 79.
E-mail address: katarina.persson@ket.kth.se (K. Persson).

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depending on the type of gas turbine, it is highly interesting to perform activity tests at elevated pressure and high gas velocities. This paper presents the results from the initial activity tests at pressures up to 15 bar and a gas velocity of 6.5 m/s for two palladium-based catalysts, one palladium only catalyst and one bimetallic catalyst with palladium and platinum. The influence of pressure and the combustion stability of each catalyst are briefly discussed.

2. Experimental

2.1. Catalyst preparation

For this study, one palladium only catalyst and one bimetallic catalyst, consisting of palladium and platinum, have been prepared by the incipient wetness technique. Both catalysts are supported on Al_2O_3 (Condea, Puralox HP 14–150). First, an aqueous solution of the corresponding metal ion/ions was prepared. For the palladium only catalyst palladium nitrate was used and for the bimetallic catalyst platinum and palladium nitrate. The alumina powder was then impregnated with the corresponding aqueous nitrate solution. Both catalyst powders were calculated to have a loading of 470 μmol metal/g, corresponding to 5 wt.% Pd on alumina. The catalyst powders were calcined at 1000 °C for 1 h. They were then mixed with ethanol, ball-milled and coated onto cordierite monoliths (400 cpsi, Corning). Two different sizes of monoliths were fabricated; one ϕ 14 mm, length 10 mm used for the lab-scale reactor and one ϕ 35 mm, length 20 mm used for the high-pressure test facility. More details regarding the catalysts are presented in Table 1.

2.2. Catalysts characterization

The surface area was determined according to the Brunauer–Emmett–Teller method by means of nitrogen adsorption at liquid N_2 temperature in a Micromeretics ASAP 2010 instrument. The dispersion of the catalysts was analysed using a Micromeritics AutoChem 2910, equipped with a thermal conductivity detector (TCD). The catalyst powder was first reduced in H_2 at 300 °C, after which CO-pulse chemisorptions was performed. For calculating the dispersion, an adsorption of one CO molecule per Pd atom was assumed. Inductive coupled plasma mass spectrometry (ICP-MS) was used to verify the amount of precious metals in the samples. The crystal phases were determined by X-ray diffraction, using a Siemens Diffraktometer D5000. The operation parameters were: Cu Kα radiation, Ni filter, 30 mA 40 kV, 2θ scanning from 20° to 80° with a step size of 0.02.

2.3. Activity tests

2.3.1. Lab-scale reactor

The activity test at atmospheric pressure was performed in a conventional tubular flow reactor. The feed had a lambda value of 4 and a space velocity of 250,000 h^{-1}. The temperature was recorded by a thermocouple placed upstream the monolith. The product gas was monitored by an online gas chromatograph (Varian 3800) equipped with a thermal conductivity detector. The activity tests were performed in a steady-state approach, with constant temperature during 30 min per step. A fresh catalyst was placed in the reactor for each test. The inlet temperature was set to 450 °C and was kept constant for 30 min, then the temperature was increased in steps of 50 °C up to 550 °C in two consecutive cycles. The methane conversion was calculated from the recorded methane content of the product gas.

2.3.2. High-pressure test facility

The high-pressure tests were performed in a custom-built test facility allowing tests to be conducted at pressures up to 35 bar and inlet temperatures up to 600 °C. The catalytic combustor, electrical heaters, fuel injection and mixing system are all located inside a pressure vessel with diameter 300 mm and height 3 m. The pressure of the air is increased by running it through a high-pressure air compressor (piston type, 40 bar and 100 g/s). In order to heat up the compressed air to the desirable temperature prior to entering the combustor, a group of electrical heaters is installed. The methane is supplied through a fuel injection system located upstream the catalyst. A series of thermocouples have been inserted to measure the temperatures at different locations in the system. The combustor section is well insulated in order to obtain nearly adiabatic conditions. The high-pressure test facility is described in more detail elsewhere [10]. The tests in this study were performed between 5 and 15 bar with a lambda value of 6.5. To facilitate the comparison between the pressure levels, the linear velocity was maintained at 6.5 m/s. A number of tests, both increasing and decreasing the pressure in steps, were performed for each operating condition in order to verify the repeatability. The results from tests in which the pressure was decreased are presented in this paper. The methane conversion was calculated by

Table 1
The compositions, BET surface area and dispersion of the two catalysts

Catalyst	Pd loading[a] (wt.%)	Pt loading[a] (wt.%)	Dispersion (%)	BET surface area (m^2/g)
Pd-Al_2O_3	4.6	–	4	102
PdPt-Al_2O_3	3.3	3.0	4	91

[a] Determined by ICP.

dividing the temperature differences over the catalysts, $T_{exit} - T_{inlet}$, by the adiabatic flame temperature rise, $T_{adiabatic} - T_{inlet}$. This way of calculating the methane conversion provides a more reliable measurement for this test facility compared to calculation based on the outlet concentration of methane. Since homogeneous combustion is possible downstream the catalyst, the concentration of methane is not entirely due to the heterogeneous combustion over the catalyst.

3. Results

3.1. Characterization

The XRD diffractograms reveal that the Pd only catalyst contains mostly PdO. The Pd-Pt catalyst showed the largest peak for metallic palladium, which was shifted towards metallic Pt, indicating an alloying effect between Pd and Pt. However, a low amount of PdO was also detected for the bimetallic catalyst. The support material for both catalysts consists of δ-Al_2O_3. As shown in Table 1, no large variation is observed in the BET surface areas or dispersions between the two samples.

3.2. Lab-scale tests

The results from the lab-scale tests for Pd-Al_2O_3 and PdPt-Al_2O_3 are presented in Figs. 1 and 2, respectively. The palladium only catalyst showed a high initial activity at 450 °C. However, as illustrated in Fig. 1, the methane conversion drops rapidly from 75% down to 17% over a 30 min time span, even though the inlet temperature was kept constant. When the inlet temperature is increased to 500 °C, the catalyst initially regains some activity, i.e. 46% conversion. However, after a few minutes the catalyst starts to lose activity again, resulting in a conversion of 18% after 30 min. By further increasing the inlet temperature to 550 °C, a slightly higher conversion is obtained. A rapid decrease in activity is observed for this step as well. The second cycle presents a markedly lower activity, where the step at 450 °C just obtains a conversion of 2%.

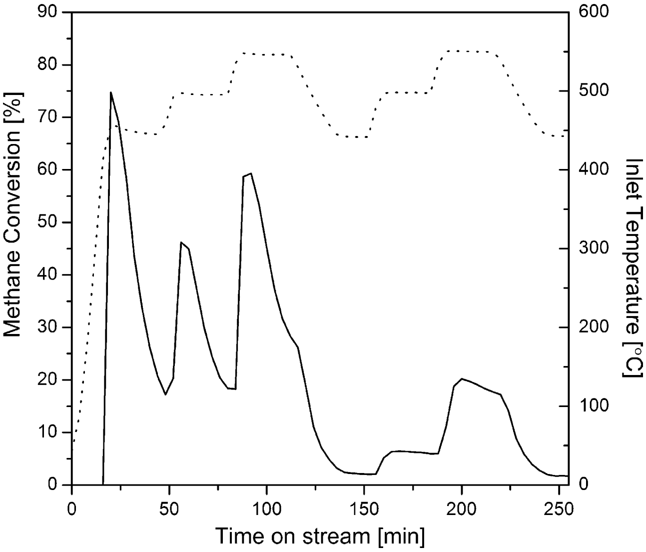

Fig. 1. A lab-scale test performed at atmospheric pressure by varying the temperature stepwise. The solid line represents the methane conversion over Pd-Al_2O_3 and the dotted line represents the inlet temperature to the catalyst.

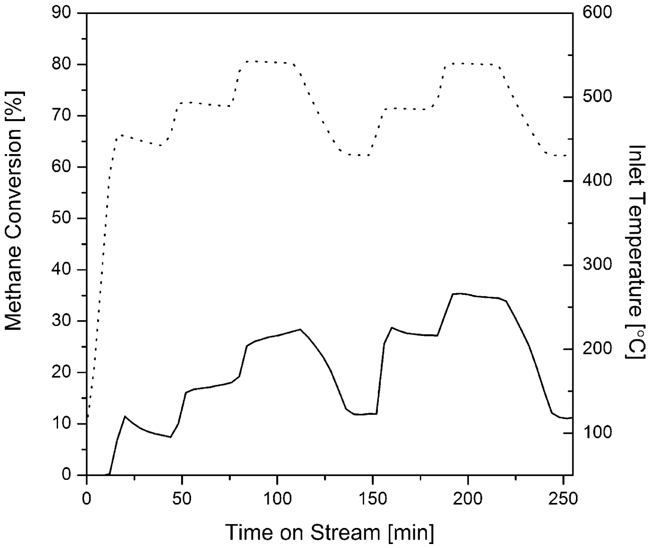

Fig. 2. A lab-scale test performed at atmospheric pressure by varying the temperature stepwise. The solid line represents the methane conversion over PdPt-Al_2O_3 and the dotted line represents the inlet temperature to the catalysts.

For the bimetallic catalyst, shown in Fig. 2, the first cycle has lower conversion than for the palladium only catalyst. In contrast, the second cycle showed much higher conversion compared to the palladium only catalyst, a conversion of 11% at 450 °C compared to 2% for Pd-Al_2O_3. It is interesting that the conversion over PdPt-Al_2O_3 is higher for the second cycle than for the first cycle. For all steps in the test PdPt-Al_2O_3 is fairly stable, with no rapid decrease in conversion and the methane conversion increases with temperature for both cycles.

3.3. High-pressure tests

For the high-pressure tests fresh catalysts were inserted in the high-pressure test facility. Prior to the tests studying the influence of pressure, the catalysts were stabilised by running them at 5 bar at 450, 500 and 550 °C, respectively, for 30 min per temperature. Similar results were found as in the lab-scale experiments at higher pressure for the palladium only catalyst, i.e. an initially high activity that falls rapidly after a short time. Furthermore, in agreement with the atmospheric tests discussed above, the bimetallic catalyst was more stable and slightly more active.

The results regarding the pressure influence are illustrated in Fig. 3. For both catalysts, the pressure was lowered from 15 down to 5 bar in steps of 2.5 bar, keeping

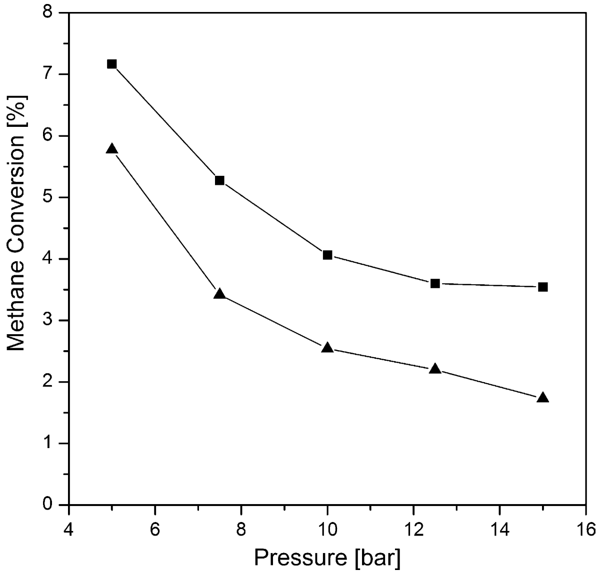

Fig. 3. The influence of pressure on the methane conversion at inlet temperature 500 °C for Pd-Al_2O_3 (▲) and PdPt-Al_2O_3 (■). The tests were conducted in the high-pressure test facility.

the inlet temperature at 500 °C. The experiments showed a decrease in methane conversion with increasing pressure. The decrease in conversion was most noticeable for the lower pressures, i.e. below 10 bar, while at higher pressures the impact was small. The two catalysts show similar trends, but the bimetallic catalyst is slightly more active, i.e. about 1.5% units higher.

4. Discussion

Supported palladium catalysts are generally known as very active catalysts for methane combustion, but the results presented in this paper show a rapid drop in methane conversion after a short operating time. Both the lab-scale reactor and the high-pressure test facility suggest this poor combustion stability over the palladium only catalyst. The lab-scale experiment presents a drop of 58% in methane conversion at 450 °C after 30 min. The activity resulting after a single temperature cycle is not sufficient to ignite methane at the inlet temperatures found in gas turbines. Conversely, the Pd-Pt catalyst maintains its activity for the lengths of time studied here. Even though its activity is lower than for the palladium only catalyst in the beginning of the tests, the bimetallic catalyst is more stable and the activity surpasses that of the palladium only catalyst in the long run. The higher stability for the Pd-Pt catalyst is in agreement with the results presented by Ersson et al. [4] and Narui et al. [5].

The superior combustion stability of the Pd-Pt catalyst reported in this paper has been explained by Narui et al. [5] and Ozawa et al. [7] as an effect of suppressed particle growth compared to the palladium only catalyst. However, the poor stability of Pd-Al_2O_3 may also be an effect of several other features. One explanation may be the water inhibition effect reported by Ciuparu et al. [11] and/or the changes into different palladium oxide species during combustion [12,13].

Most activity tests published for catalytic combustion purposes have been performed at atmospheric pressure. Since a gas turbine is working at a pressure of up to 30 bar it is desirable to investigate the pressure impact on the combustion activity. Therefore, the two catalysts were tested at elevated pressures in a high-pressure reactor. Similar results were obtained from this test facility as for the lab-scale reactor. Hence, the more stable behaviour of the bimetallic catalyst was confirmed at higher pressure as well. However, slightly different operating conditions were used due to restrictions of the test facilities. Therefore, the absolute numbers of the methane conversion obtained from the two test facilities were not directly comparable.

When considering the pressure influence on methane conversion, both catalysts showed similar trends when the pressure was lowered from 15 to 5 bar, i.e. the methane conversion decreases with increasing pressure. The impact of pressure appears to be more perceptible at lower pressures than for pressures above 10 bar. Since both catalysts showed similar trends, the pressure impact seemed not to be affected by the type of catalyst used. Carroni et al. [14] have also investigated the pressure influence on the activity of palladium catalysts. Their experimentally measured temperature difference over the catalyst is in agreement with our results. They suggest that pressure has both negative and positive effects on the combustion, resulting in larger mass troughput and a higher surface reaction rate at elevated pressure. Further, the maximum achievable conversion over the catalyst decreases with increasing pressure due to growing mass-transport limitations. Hence, the pressure impact is not just a catalyst matter, but also a question of mass-transport restrictions. The two catalysts tested in this study present different activities. Therefore, the maximum achievable conversion is probably not reached for at least the palladium only catalyst. A more active catalyst could therefore increase the conversion, but not more than the mass-transport limitations allow. Further studies, including experimental tests and CFD modelling, are needed in order to clarify the pressure impact.

5. Conclusions

The results showed that a bimetallic palladium-platinum catalyst is more stable during methane combustion over the time period tested in this study compared to a palladium only catalyst. This is confirmed both in lab-scale atmospheric tests as well as in high-pressure experiments at pressure up to 15 bar, i.e. more realistic operating conditions in gas turbine applications. The influence of pressure on the combustion activity was studied as well. The methane conversion decreases when pressure was increased. However, the impact was more pronounced at the lower pressures, whereas the influence levels out for pressures above 10 bar.

Acknowledgements

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