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Catalytic combustion of methane over bimetallic catalysts a comparison between a novel annular reactor and a high-pressure reactor

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Abstract

The effects of adding a co-metal, Pt or Rh, to Pd/γ-Al_2O_3 catalysts were studied with respect to the catalytic activity for methane combustion and compared to a Pd/γ-Al_2O_3 catalyst, using both a pressurized pilot-scale and a lab-scale annular reactor. Temperature programmed oxidation (TPO) experiments were also carried out to investigate the oxygen release/uptake of the catalyst materials. Palladium showed an unstable behavior both in the pilot and lab-scale experiments at temperatures well below the PdO to Pd transformation. An addition of Pt to Pd stabilized, and in some cases increased, the catalytic activity for methane combustion.

The TPO experiments showed that the oxygen release peak was shifted to lower temperatures even for low additions of Pt, i.e. Pd:Pt = 2:1. For additions of rhodium only small beneficial effects were seen. The steady-state behavior of the lab-scale annular reactor correspond well to the pressurized pilot-scale tests.

Keywords: Palladium; Bimetallic; Catalytic combustion; Methane; High pressure

1. Introduction

One of the main hurdles to overcome before implementing catalytic combustion in a gas turbine combustor is the ignition of the fuel at compressor outlet temperatures. Several concepts for achieving this have been proposed, some of them require engineering solutions with additional components such as preburners and electrical heaters. However, this adds to the complexity of the gas turbine and in the case of preburners it is also a source of nitrogen oxide emissions. Hence, it would be preferable to have a catalyst with sufficient activity to ignite the fuel at the compressor outlet temperature—at least at full load. This means that the catalyst has to be active in the 350–550 °C temperature range depending on the type of gas turbine used. Natural gas, with methane as the main component, is the fuel in most applications considered for catalytic combustion. Palladium is often used as an oxidation catalyst for methane and has been studied extensively over the years [1–4]. However, the use of pure palladium catalysts has some drawbacks. The transformation from palladium oxide to palladium, and the hysteresis depend on the difference in reformation

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temperature, induces instabilities in the performance of the catalytic combustor. The formation, the activity, and the nature of the different phases of the PdO/Pd system are still not fully understood. Recent work by Groppi et al. [5,6] has shown the possible occurrence of two different types of palladium oxide with different activity for methane oxidation. The methane activity was measured at fixed temperatures from 450 to 550 °C, showing a decrease in activity with time at temperatures well below the PdO/Pd transformation, similar results are reported in the present study. The first PdO species is supposed to be transformed into the second PdO species as the temperature increases, however the change occurs at lower temperatures than for the PdO/Pd transformation. The higher activity of the first PdO species led to the hypothesis that it could be a PdO in boundary contact with metallic Pd. Pfefferle and co-workers [7,8] have proposed this mixed form to be especially active for methane combustion. Several authors have also suggested the combustion of methane to be a dual site mechanism involving one reduced site for the dissociation of methane, either an oxygen vacancy in the PdO lattice [9] or metallic Pd [10,11], and an oxidized site for the oxidation step. This phenomenon, together with sintering and poisoning of the catalyst, gives rise to a very complex behavior of the catalyst, especially in a gas turbine environment.

In order to stabilize activity, addition of another metal to the palladium, forming a bimetallic catalyst, has been proposed. The use of noble metals such as Pt, Rh, Ru, etc. as co-metals has been studied for many applications including both hydrogenation and oxidation reactions. Coq and Figueras [12] have reviewed the influence of the co-metal on catalyst performance in bimetallic catalysts with focus on hydrogenation reactions. They concluded that the effect could be interpreted as a geometric effect, electronic effect or the presence of mixed sites, depending on both the co-metal and the reaction. The oxidation of CO and hydrocarbons over Pd–Pt catalysts has been examined by Skoglundh et al. [13] showing an increased activity even at very low additions of platinum. Narui et al. [14] have studied the effect of adding Pt to Pd using TEM, concluding that the Pt increases the catalytic activity for methane combustion and decreases the sintering of the metal particles. The addition of a second metal, such as Ru, could also improve the resistance to sulfur poisoning [15]. Rhodium has also been investigated by several authors with contradictory results. Ryu et al. [15] found no beneficial effect of the addition of Rh, while Rassoul et al. [16] have shown a small positive effect of the Rh addition. Tochihara and Ozawa [17] reported an increase in the stability of the PdO with the addition of Rh that resulted in less oscillation in conversion over time at high temperatures.

The preparation method has significant influence on the activity and dispersion of bimetallic palladium catalysts [18,19]. Pieck et al. [19] have shown that bimetallic catalysts prepared from chlorine-free precursors have much higher activity than those prepared form chlorine-containing precursors. In this study an incipient wetness technique using co-impregnation of metal nitrates has been used, in order to avoid the negative effect of chlorine.

Two different reactors have been used. A pressurized pilot-scale reactor and a lab-scale annular reactor have been used, allowing high gas velocities, 15 and 1.1 m/s, respectively. Within the pilot-scale reactor, tests could be run under conditions similar to a real gas turbine combustor, allowing the effect of pressure to be studied.

2. Experimental

2.1. Preparation of the catalysts

The catalyst powders used for detailed characterization and lab-scale activity tests were prepared by the incipient wetness technique. First, an aqueous solution of the metal ion/ions was prepared. For this purpose palladium nitrate, rhodium nitrate [both Johnson Matthey], platinum nitrate [Merck] were dissolved in water and carefully mixed with alumina powder [PURALOX HP-14/150, Condea]. The powders were then dried at 300 °C and the procedure was repeated in order to achieve the desired metal loading. The lab-scale catalyst powders had a total loading of 470 μmol metal per gram, which corresponds to 5 wt.% of palladium on the alumina. The resulting powders were thereafter calcined at 1000 °C for 1 h. The catalyst powders were then ball-milled and coated onto γ-alumina tubes ($Ø_{outer} = 4$ mm $Ø_{inner} = 2$ mm) [Keranova] with a catalyst layer of 20 mm in length and a thickness of about 20 μm. The coated tubes were calcined

Table 1
The different catalysts used in the lab-scale experiments

Catalyst abbreviation	Pd:Metal mole-ratio
PdPd	Pd = 1:0
PdPt21	Pd:Pt = 2:1
PdPt11	Pd:Pt = 1:1
PdPt12	Pd:Pt = 1:2
PdRh21	Pd:Rh = 2:1
PdRh11	Pd:Rh = 1:1
PdRh12	Pd:Rh = 1:2

at 1000 °C, 2 h. A summary of the prepared catalysts is found in Table 1.

The catalysts used for the pilot-scale tests were supplied externally, and the active powder was supported onto a Fecralloy metal honeycomb. The geometry of the honeycomb was similar to that of the A-series tests of Carroni et al. [20]. Within these catalysts the noble metals were supported onto alumina. Two different catalysts were tested, one with palladium only and one bimetallic Pd–Pt. The monoliths had alternatively coated channels to avoid overheating the active phase.

2.2. Characterization

The crystal-phases were identified by powder X-ray diffraction (XRD) using a Siemens Diffractometer 5000 scanning 2θ from 10° to 90° using monochromatic Cu Kα radiation. The crystal-phases were identified using JCPDS files. Temperature programmed oxidation (TPO) measurements were performed using a Micrometrics *AutoChem* 2910 instrument. Approximately, 100 mg of sample was loaded for each measurement. A flow of 20 cm^3/min (at STP) of 5 v/v% O_2 in He mixture was introduced over the sample. Three consecutive heating–cooling cycles from 300 to 900 °C were performed with a heating rate of 10 °C/min.

2.3. Lab-scale activity tests

The transient activity tests were carried out in an annular reactor first proposed by McCarty [1] consisting of a quartz tube containing a concentric α-alumina tube on which a thin catalyst layer is deposited. The reactor is shown in Fig. 1. A thermocouple of type K was placed inside the tube measuring the catalyst temperature. This configuration allows for high gas velocities with a minimal pressure drop. The annular reactor is described in detail elsewhere [21]. In the present experiments the gas flow was 1000 ml/min with 1.5% methane in air. The activity tests were conducted with two consecutive heating and cooling cycles at temperatures from 100 up to 950 °C at a rate of 5 °C/min. Lab-scale activity tests were also conducted to study the steady-state activity of the catalysts. Three different catalysts were chosen for these measurements, i.e. Pd5%, PdPt11, and PdRh11. During these tests the temperature was held at constant temperature for given periods of time.

2.4. Pilot-scale testing

The pilot-scale test was performed in a high-pressure test rig at ALSTOM Power in Switzerland. The test rig is described in detail elsewhere [20]. The rig

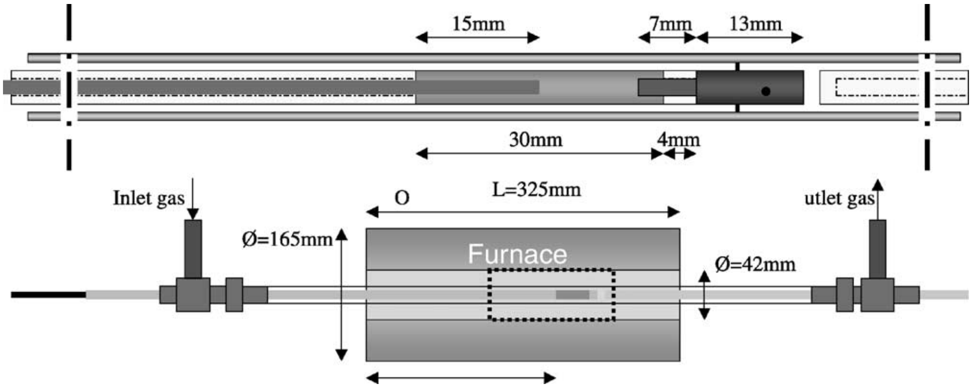

Fig. 1. The annular reactor used in the study.

consisted of four main parts, the air pre-heaters, the fuel injection and mixing section, the catalyst test section and the burnout zone. The catalyst, 35 mm in diameter and 64 mm in length, was mounted in a steel cylinder with thermocouples located both up and down stream of the catalyst. The conversion was calculated form the temperature rise over the catalyst compared with the adiabatic flame temperature of the gas mixture. The pre-heaters allowed the inlet air to be heated up to 550 °C. Down stream the catalyst, the unburned fuel was combusted in a homogeneous combustion zone, a sudden area expansion created a recirculation zone that acted as a flame-holder. The pilot-scale tests reported in this paper were all carried out at 5 bar with an inlet gas velocity of 15 m/s and $\lambda = 2.5$ (air:fuel ratio). In the tests the temperature was increased in steps and kept constant over longer periods of time (i.e. several minutes).

3. Results

3.1. TPO measurements

The TPO plots are shown in Fig. 2a–c. The Pd5% catalyst shows a large peak at 810 °C surrounded by two smaller peaks, which all correspond to the decomposition of the palladium oxide. Groppi et al. [5,6]

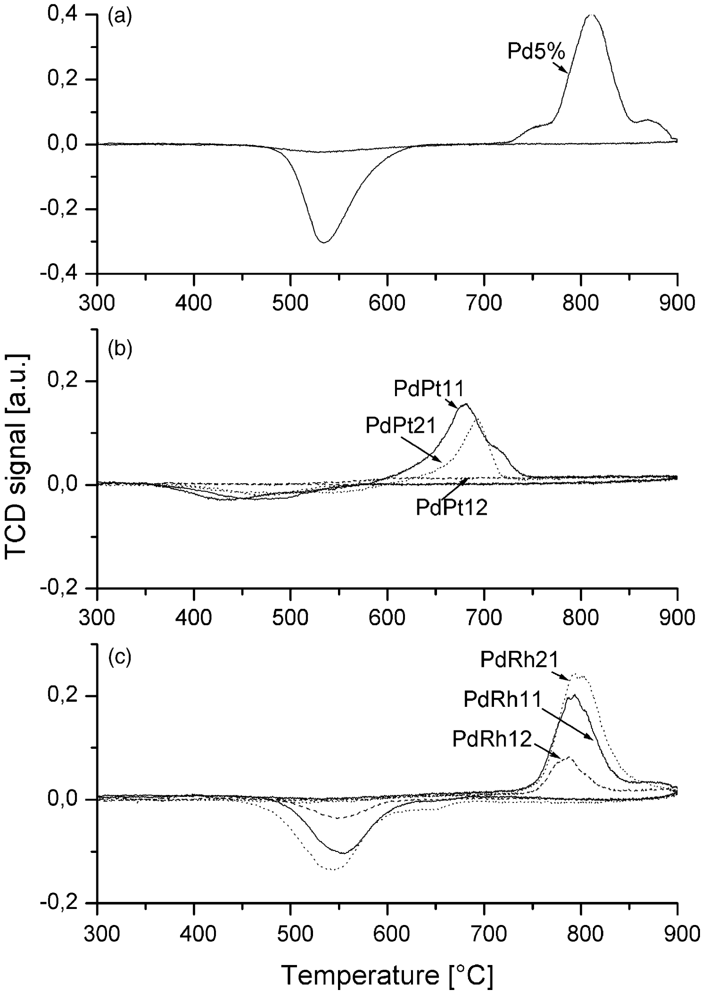

Fig. 2. TPO plots for (a) Pd5% catalyst; (b) Pd–Pt catalysts; (c) Pd–Rh catalysts.

have argued that two of these peaks are the result of two different forms of palladium oxide. When the temperature is lowered, a single re-oxidation peak occurs at 530 °C.

The Pd/Rh catalysts show only slightly different behavior. While the main decomposition peak has shifted towards a lower temperature, i.e. 790 °C, the re-oxidation temperature is similar to that observed for the Pd5% catalyst.

In contrast, the Pd/Pt catalysts show very different oxidation behavior as compared to the Pd5% catalyst. The decomposition temperature is shifted to a much lower temperature even for the PdPt21 catalyst. As the platinum content increases, the decomposition shifts towards an even lower temperature. For the PdPt11 the release of oxygen appears to be a two-step process. The re-oxidation is also shifted towards a lower temperature and, more importantly, the sizes of the re-oxidation peaks are much smaller that for both the Pd–Rh and the Pd5% catalysts and the re-oxidation occurs over a wide range of temperature.

3.2. Lab-scale test

3.2.1. Activity tests

The transient behavior of the catalysts was studied during two consecutive heating/cooling cycles. The conversion of methane over the catalysts during the second cycle is shown in Figs. 3 and 4. For the first cycles the conversion over the catalysts was generally

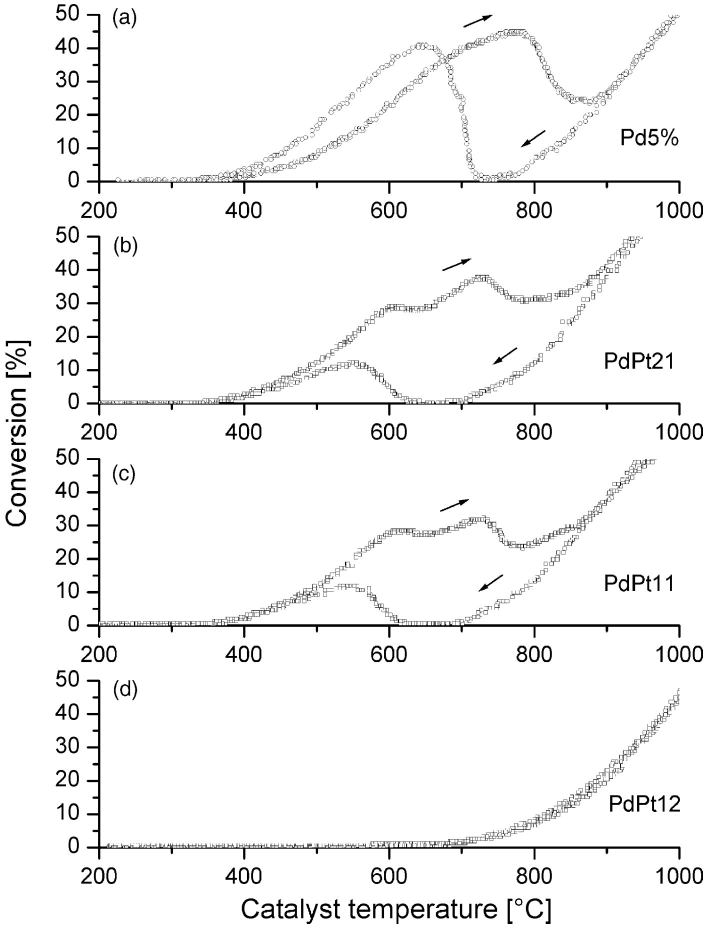

Fig. 3. Lab-scale catalytic activity for the Pd–Pt catalysts. Reaction conditions: 5 °C/min temperature ramp; 1.5% methane in air; gas velocity 1.1 m/s. (a) Pd5% (reference catalyst); (b) PdPt21; (c) PdPt11; (d) PdPt12.

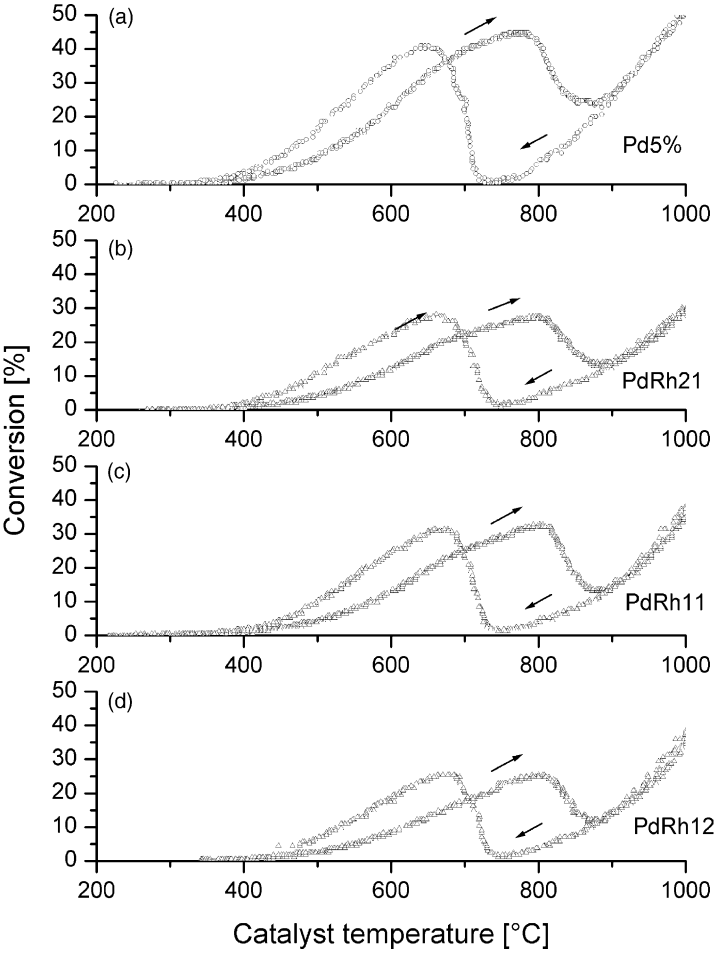

Fig. 4. Lab-scale catalytic activity for the Pd–Rh catalysts. Reaction conditions: 5 °C/min temperature ramp; 1.5% methane in air; gas velocity 1.1 m/s. (a) Pd5% (reference catalyst); (b) PdRh21; (c) PdRh11; (d) PdRh12.

lower than for the second cycles. The Pd5% cycle is shown as a reference catalyst, and indicates the typical hysteresis of PdO to Pd transformation. A local maximum is reached at 775 °C corresponding to the decomposition of PdO to Pd, followed by a minimum at 875 °C. For the cooling, a maximum is reached at 645 °C corresponding to the reformation of PdO.

For the bimetallic Pd–Pt catalysts (Fig. 3a–d) a rather different behavior was observed. The PdPt21 and PdPt11 showed similar performances. During heating, instead of having a pronounced maximum as for the Pd5% catalyst, two local maxima are observed. The activity is slightly higher for the Pd–Pt catalysts up to the first maximum at 610 °C, the second maximum occurs at 730 °C. After 610 °C, the activity is higher for the Pd5% catalyst up to 820 °C, where the conversion of the Pd–Pt catalysts increases. A local maximum is reached during the cooling at a lower temperature, i.e. 550 °C, than for the Pd5% catalyst and the conversion is considerably lower. A completely different behavior is observed for the PdPt12 catalyst, where the light-off occurs at 700 °C. Moreover, no hysteresis and no local maximum or minimum is found during the heating/cooling cycles.

The Pd–Rh bimetallic catalysts (Fig. 4a–d) showed similar behavior as the Pd5% catalyst. However, the conversions were lower than for the Pd5% catalyst.

The highest activity of the Pd–Rh catalyst was found for the PdRh11 catalyst.

3.2.2. Lab-scale steady-state tests

For steady-state measurement within the annular reactor, three catalysts were chosen: PdPt11, PdRh11, and Pd5% as a reference catalyst. The results from the steady-state tests are shown in Figs. 5–7. For the lower temperature range 300–400 °C, all catalysts showed low but stable conversion. At 450 °C there are a major differences between the three catalysts. The conversion over Pd5% drops rapidly from 26 to 14% over a time span of 50 min. In contrast PdPt11 showed a small increase in conversion, however the conversion was lower than for Pd5%, i.e. around 8%. The conversion over PdRh11 was very low at 450 °C. At a furnace

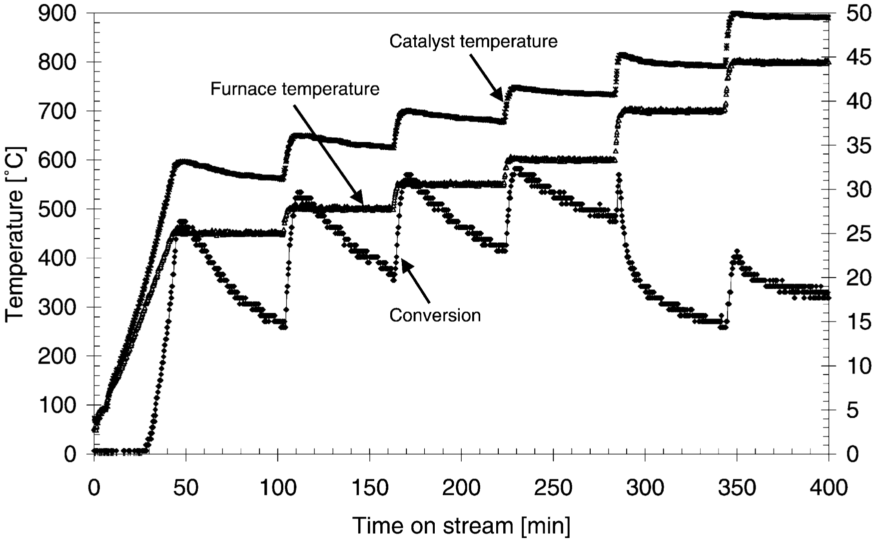

Fig. 5. Lab-scale steady-state test for Pd5%. Reaction conditions: 1.5% methane in air; gas velocity 1.1 m/s.

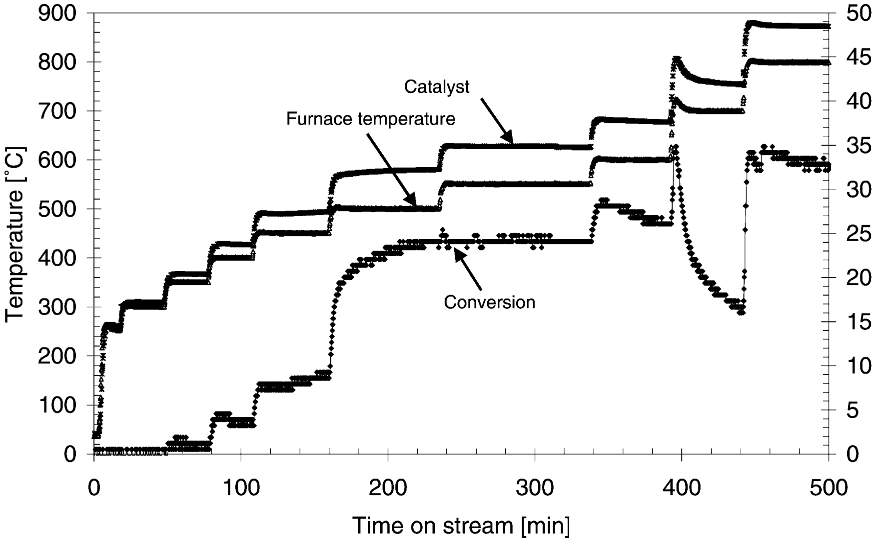

Fig. 6. Lab-scale steady-state test for PdPt11. Reaction conditions: 1.5% methane in air; gas velocity 1.1 m/s.

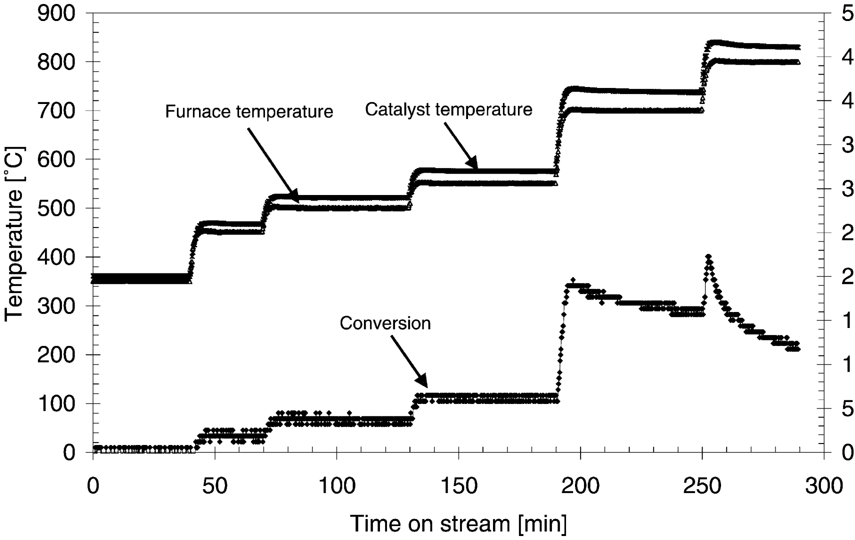

Fig. 7. Lab-scale steady-state test for PdRh11. Reaction conditions: 1.5% methane in air; gas velocity 1.1 m/s.

temperature of 500 °C both Pd5% and PdRh11 showed similar behavior as for 450 °C, although with a slightly higher conversion. However, PdPt11 showed a rapid increase in conversion up to 24% after 70 min, surpassing the Pd5% catalyst in conversion. At 550 °C the conversion of PdPt11 remains constant at 24%, while Pd5% showed the same rapid increase followed by a steep decline in conversion. PdRh11 still shows a stable but low conversion, i.e. 4%. When the furnace temperature was increased to 600 °C the behavior of the PdPt11 catalyst changes to a behavior more similar to that of Pd5% catalyst, though the drop in conversion is less pronounced. For PdRh11 the conversion remains stable but low. At 700 °C the conversion over both PdPt11 and Pd5% drops rapidly, however for PdRh11 the conversion increases rapidly up to 20% followed

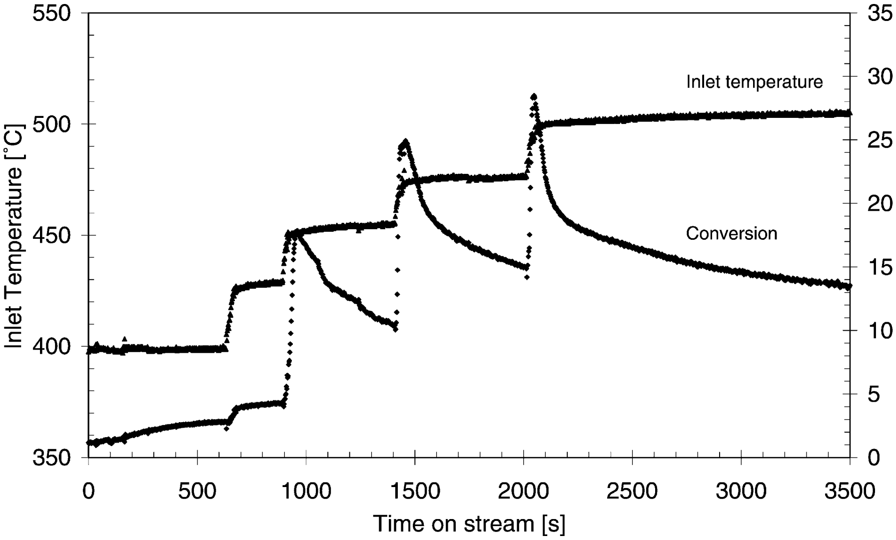

Fig. 8. Pilot-scale test using a fresh palladium on alumina catalyst. Test conditions: 5 bar; gas velocity 15 m/s; air to fuel ratio 2.5.

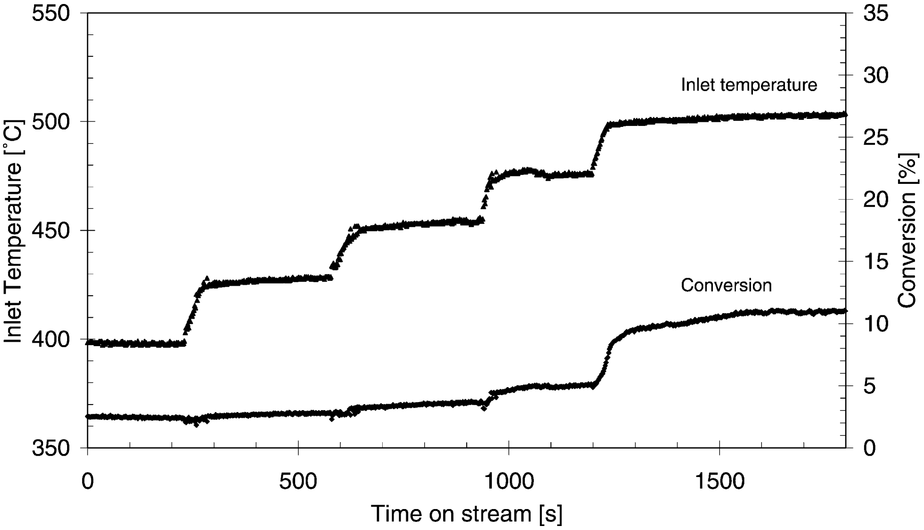

Fig. 9. Pilot-scale test using an aged palladium on alumina catalyst. Test conditions: 5 bar; gas velocity 15 m/s; air to fuel ratio 2.5.

by a slow decrease to 16%. It should be taken in to account that the differences in conversions over the different catalysts give rise to a difference in actual catalyst temperature, so that Pd5% and PdPt11 have an initial catalyst temperature above 800 °C, while PdRh11 only sees 750 °C as a maximum temperature at 700 °C furnace temperature. At 800 °C furnace temperature the conversion over PdRh11 shows a similar behavior as Pd5% and PdPt11 at 700 °C. For Pd5% the conversion increases to 23% then decreasing to 18% over a 50 min time span. PdPt11, however, increase the conversion up to 34% and remained constant over the same time period.

3.3. Pilot-scale test

The results for the pilot-scale tests are shown in Figs. 8–12. For the fresh palladium catalyst (Fig. 8)

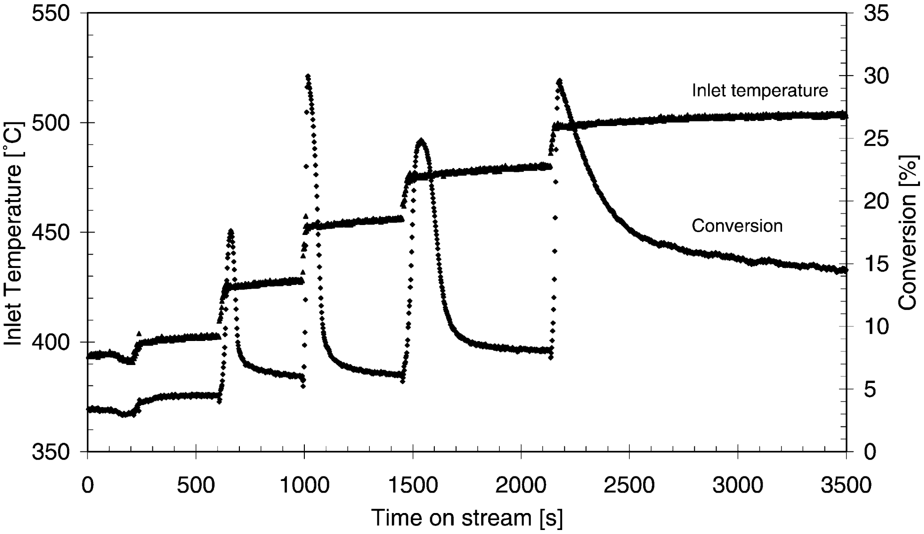

Fig. 10. Pilot-scale test for aged palladium on alumina catalyst, after being exposed to ambient air for 1 week. Test conditions: 5 bar; gas velocity 15 m/s; air to fuel ratio 2.5.

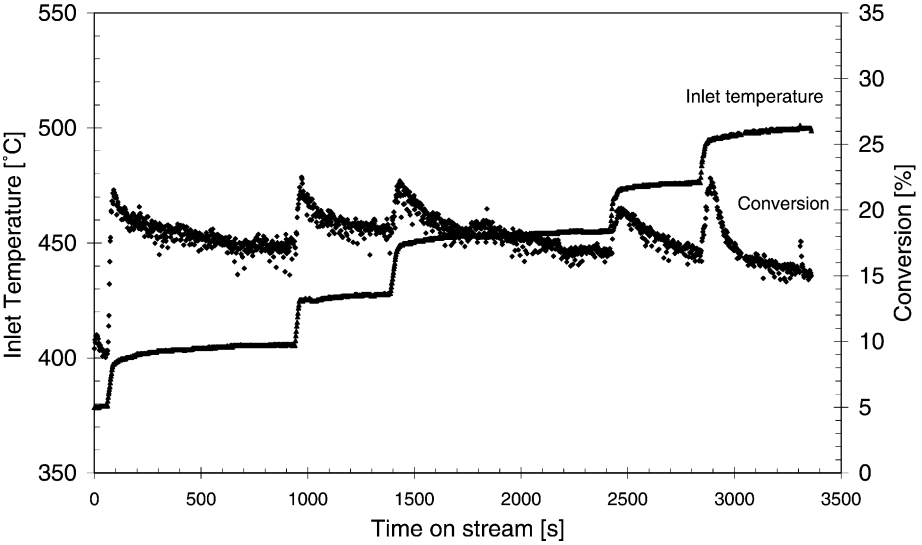

Fig. 11. Pilot-scale test using fresh Pd–Pt on alumina catalyst. Test conditions: 5 bar; gas velocity 15 m/s; air to fuel ratio 2.5.

a rapid increase in activity occurs after each change in inlet temperature for temperatures over 425 °C. A steep fall in conversion occurs within the first couple of minutes, after which the decrease levels off. Fig. 9 shows the consecutive second run with the same palladium catalyst. The spikes in conversion that were found for the fresh catalyst have vanished and the conversion remains stable over time for each inlet temperature window. Moreover, the conversion is significantly lower than for the fresh catalyst. An interesting phenomenon (Fig. 10) was observed when the catalyst was left for 7 days in ambient air and re-tested. The initial spikes in conversion that were observed for the fresh catalyst reoccur, however, the decrease is much faster then for the fresh catalyst and the conversion is lower.

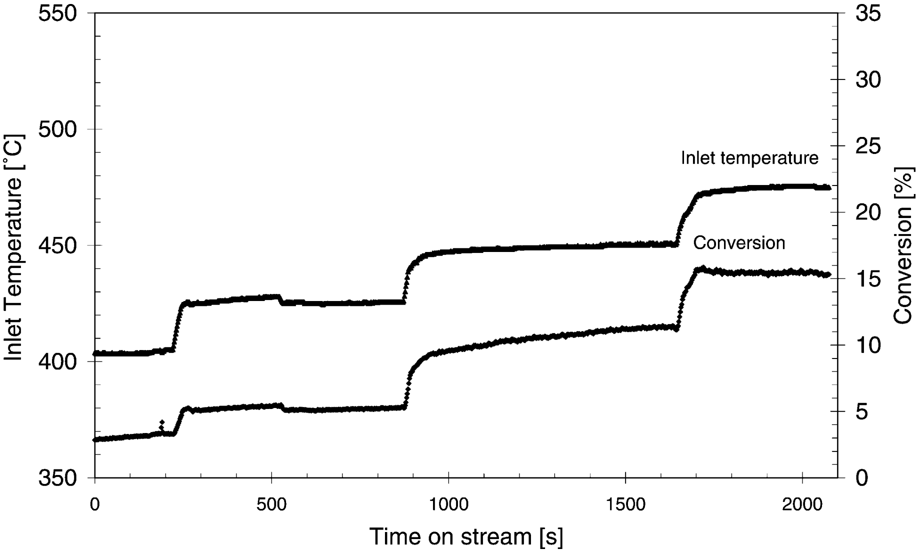

Fig. 12. Pilot-scale test using an aged Pd–Pt on alumina catalyst. Test conditions: 5 bar; gas velocity 15 m/s; air to fuel ratio 2.5.

For the fresh Pd–Pt catalyst (Fig. 11) the behavior is different from that of the Pd catalyst. The spikes in conversion are much less pronounced and the decreases in conversion are also lower. The conversion for the Pd–Pt catalysts remained at a high level, i.e. 15%, over the whole temperature range from 400 to 500 °C, while for the Pd catalyst the conversion increased with each increase in temperature. For the second consecutive run over the Pd–Pt catalyst (Fig. 12) the behavior is more similar to the corresponding Pd-catalyst but with a higher conversion. Unlike the fresh Pd–Pt catalyst the conversion increases with increased inlet temperature.

4. Discussion

The pilot-scale tests using palladium on alumina catalyst clearly show the need for more stable catalytic materials. The rapid decrease in activity, even at low inlet temperatures shows the difficulty in igniting methane and in keeping the conversion at a high level without preheating the gas to temperatures above 500 °C. The decrease in activity occurs at a temperature below the PdO to Pd transformation range. This is also observed in the lab-scale experiments, where the decrease in activity occurs at an inlet temperature of 450 °C corresponding to a catalyst temperature of 600 °C, which is below the decomposition temperature of the PdO found in the TPO experiments. The drop in activity connected to the PdO to Pd transformation is clearly visible in the lab-scale experiments showing a major decrease in activity at a catalyst temperature of around 800 °C. The decrease at low temperature is probably connected to some other phenomenon than the PdO to Pd transformation. Groppi et al. [5,6] have proposed the occurrence of two different types of palladium oxides that have different thermal stabilities, one being a low temperature form, that is stable up to around 550 °C, i.e. much lower than the PdO to Pd transformation temperature.

The nature and activity of the different types of PdO have been studied by several authors and are still under discussion [3–9]. The decrease in activity could also be connected to the sintering of PdO particles, thereby decreasing the dispersion [14]. However, for the aged catalysts in the pilot-scale tests, the conversion remains stable over time although at a lower level than for the fresh catalysts. This might indicate that the reformation of a more active form of PdO or the re-dispersion of the PdO particles does not occur between the different test runs. Interesting to note is that the catalyst regains some of its initial behavior after being exposed to ambient atmosphere for a week, however the decrease in activity is faster, indicating less amount of highly active palladium being re-formed.

The addition of platinum to the palladium catalyst induced a remarkable increase in stability of the catalyst in the low-temperature region. The pilot-scale tests show only a small decrease in activity in the low temperature region and the activity of the aged catalyst was significantly higher than for the palladium catalyst. This was also seen in the lab-scale steady-state test, during which the conversion remained constant or even increased with time. The TPO experiments shows that the PdO to Pd transformation occurs at a lower temperature compared to the Pd catalyst, which was confirmed in the lab-scale tests. The activity above the transformation temperature is higher for the Pd–Pt catalysts. The amount of Pt added to the Pd had an effect on the TPO decomposition peak, where the PdPt11 catalyst showed the largest oxygen release and also showed signs of a double peak. Although PdPt21 released less oxygen, the conversion was higher for methane combustion. In contrast, for PdPt12 the Pd-like behavior completely disappeared and was changed to Pt-like behavior with no release of oxygen in the TPO and no activity at low temperatures for methane combustion.

The improved stability of the Pd–Pt catalysts has been explained to be the result of increased resistance towards sintering of the PdPt particles compared to the Pd particles [14]. The improved activity at high temperature, i.e. above 800 °C, could be due to the contribution of the Pt-metal activity.

Rhodium additions had, except for a diluting effect as the Pd content of the catalyst decreases with increasing Rh content, a small effect on the performance of the palladium catalysts. For rhodium the TPO showed that oxygen release from the bimetallic Pd–Rh catalysts was similar to that of Pd in temperature, however the amount of oxygen released decreased with increasing Rh content. This implies that the Rh only dilutes the Pd and does not affect the decomposition of the

PdO. The same effect occurs in the transient activity tests. Of the Pd/Rh catalysts, PdRh11 thus showed the highest conversion of methane, although still lower than for Pd5%. The steady-state tests showed that the thermal stability of the Pd–Rh catalysts was better than for the Pd-catalyst, however, the conversion was much lower than for both the Pd and the Pd–Pt catalyst.

In the lab-scale annular reactor, the reactants flow with a high linear velocity and negligible pressure gradients under laminar conditions. Hence, activity tests in the lab-scale annular reactor can be extended to significantly higher temperatures without reaching complete conversion [22]. Comparable conditions are found in the catalyst channels in the high-pressure pilot-scale tests, with high inlet velocities and alternatively coated channels cooling the catalyst surface and keeping the conversion low. The lab-scale annular reactor steady-state experiments correspond well to the pressurized pilot-scale tests, both showing an unstable behavior of palladium at temperatures well below the PdO to Pd transformation. (Figs. 5 and 8). The conversion was also in the same range for both reactors stressing further the similarities between the data received from the annular reactor and the pilot-scale reactor.

5. Conclusions

Palladium shows an unstable behavior both in lab-scale steady-state tests as well as in pressurized pilot-scale tests, with rapidly diminishing activity after each inlet temperature increase. The instabilities started to occur at temperatures well below the temperature for the PdO to Pd transformation and have to be connected to some other phenomenon, e.g. change in nature of the PdO or sintering of the metal particles.

The addition of Pt to the Pd increased the stability and in some cases increased the catalytic activity for methane combustion. This was verified both in the pilot-scale and in the lab-scale tests. Moreover, TPO showed that the oxygen release for Pd–Pt occurs at lower temperature than for pure Pd. In the lab-scale transient activity tests the Pd–Pt catalysts generally showed a similar performance as the Pd catalyst. However, for Pd:Pt with a ratio of 1:2 a platinum-like behavior was observed.

The addition of Rh to Pd did not seem to give a positive benefit, though a small stabilizing effect was observed in some cases. The activities of the Pd–Rh catalysts were lower than for the Pd catalyst.

The annular reactor with low conversions at high temperatures proved to be a viable design to mimic the behavior of a catalyst under conditions closely resembling a gas turbine combustor.

Acknowledgements

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References

[1] J.G. McCarty, Catal. Today 26 (1995) 283.

[2] R.J. Farrauto, M.C. Hobson, T. Kennelly, E.M. Waterman, Appl. Catal. A 81 (1992) 227.

[3] J.E. Baker, R. Burch, S.E. Golunski, Thermochim. Acta 142 (1989) 329.

[4] R.B. Anderson, K.C. Stein, J.J. Feenan, L.E.J. Hofer, Ind. Eng. Chem. 53 (1961) 809.

[5] G. Groppi, C. Cristiani, L. Lietti, P. Forzatti, in: A. Corma et al. (Eds.), Studies in Surface Science and Catalysis, Vol. 130, Elsevier, Amsterdam, 2000, p. 3801.

[6] G. Groppi, G. Artioli, C. Cristiani, L. Lietti, P. Forzatti, in: E. Iglesia et al. (Eds.), Studies in Surface Science and Catalysis, Vol. 136, Elsevier, Amsterdam, 2001, p. 345.

[7] A.K. Datye, J. Bravo, T.R. Nelson, P. Atanasova, M. Lyubovsky, L. Pfefferle, Appl. Catal. A. 198 (2000) 176.

[8] M. Lyubovsky, L. Pfefferle, Appl. Catal. A. 173 (1998) 107.

[9] K. Fujimoto, F.H. Ribeiro, M. Avalos-Borja, E. Iglesia, J. Catal. 179 (1998) 431.

[10] S.C. Su, J.N. Carstens, A.T. Bell, J. Catal. 176 (1998) 125.

[11] J.N. Carstens, S.C. Su, A.T. Bell, J. Catal. 176 (1998) 136.

[12] B. Coq, F. Figueras, J. Mol. Catal. A. 173 (2001) 117.

[13] M. Skoglundh, L.O. Löwendahl, J.-E. Otterstedt, Appl. Catal. 77 (1991) 9.

[14] K. Narui, H. Yata, K. Furuta, A. Nishida, Y. Kohtoku, T. Matsuzaki, Appl. Catal. A 179 (1999) 165.

[15] C.K. Ryu, M.W. Ryoo, I.S. Ryu, S.K. Kang, Catal. Today 47 (1999) 141.

[16] M. Rassoul, F. Gaillard, E. Garbowski, M. Primet, J. Catal. 203 (2001) 232.

[17] Y. Tochihara, Y. Ozawa, in: Proceedings of the Fourth International Workshop on Catalytic Combustion, San Diego, Paper CGT3, April 1999, 14–16.

[18] C. Micheaud, P. Marécot, M. Guérin, J. Barbier, Appl. Catal. A 171 (1998) 229.

[19] C.L. Pieck, C.R. Vera, E.M. Peirotti, J.C. Yori, Appl. Catal. A 226 (2002) 281.

[20] R. Carroni, T. Griffin, J. Mantzaras, M. Reinke, Catal. Today 83 (2003) 157–170.

[21] D. Papadias, U. Würtenberger, L. Edsberg, P. Björnbom, Chem. Eng. Sci. 57 (2002) 749.

[22] A. Beretta, P. Baiardi, D. Prina, P. Forzatti, Chem. Eng. Sci. 54 (1999) 765.