Stability of palladium-based catalysts during catalytic combustion of methane: The influence of water

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Abstract

The stability of methane conversion was studied over a Pd/Al₂O₃ catalyst and bimetallic Pd–Pt/Al₂O₃ catalysts. The activity of methane combustion over Pd/Al₂O₃ gradually decreased with time, whereas the methane conversion over bimetallic Pd–Pt catalysts was significantly more stable. The differences in combustion behavior were further investigated by activity tests where additional water vapor was periodically added to the feed stream. From these tests it was concluded that water speeds up the degradation process of the Pd/Al₂O₃ catalyst, whereas the catalyst containing Pt was not affected to the same extent. DRIFTS studies in a mixture of oxygen and methane revealed that both catalysts produce surface hydroxyls during combustion, although the steady state concentration on the pure Pd catalyst is higher for a fixed temperature and water partial pressure. The structure of the bimetallic catalyst grains with a PdO domain and a Pd–Pt alloy domain may be the reason for the higher stability, as the PdO domain appears to be more affected by the water generated in the combustion reaction than the alloy. Not all fuels that produce water during combustion will have stability issues. It appears that less strong binding in the fuel molecule will compensate for the degradation.

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1. Introduction

Catalytic combustion of methane has attracted attention both in the field of emission control [1,2] and power generation in gas turbines [3]. Methane is an undesirable emission from natural gas-powered vehicles due to its high global warming potential. Emissions of methane could be decreased using catalytic exhaust converters. Catalytically stabilized combustion can also be used in gas turbine combustors. This combustion technique is attractive because it offers the potential of ultra-low NOₓ levels, which is difficult to achieve with other conventional techniques. Since stationary gas turbines most often are powered by natural gas, degree of methane conversion becomes essential.

Palladium catalysts are renowned for their high activity in methane combustion and have been studied a great deal over the years [4–6]. However, the drawback with these catalysts is their poor stability, resulting in severely decreasing activity during operation [7–12]. No clear consensus regarding the cause for the deactivation has been reached in the literature. Narui et al. [8] have explained the poor stability by sintering of the PdO particles during operation. However, this explanation has been rejected by others that have shown that dispersion does not change considerably upon aging [13]. The reason for the loss in conversion has also been attributed to inhibition from the water generated during the oxidation process [14–20]. The cause of the water inhibition is suggested to be inactive hydroxyls groups being formed on the catalysts surface, which block access to the PdO sites for methane dissociation. Therefore, if water inhibition is the cause for deactivation, it is important to find a way to improve the water resistance of the palladium catalyst.

Several studies have shown that the stability of conversion is considerably improved by adding platinum to the supported palladium catalysts [8–12,21]. This is confirmed both for longer durations and at higher pressures [12,22]. Even though water inhibition may be the reason for deactivation of monometallic catalysts, few studies have investigated how the water affects
bimetallic Pd–Pt catalysts. In the present study, both Pd and bimetallic Pd–Pt catalysts have been investigated by means of different activity tests and DRIFTS measurements in order to explain the water effect.

2. Experimental

2.1. Catalyst preparation

A monometallic palladium catalyst and two palladium–platinum catalysts were prepared for this study. Alumina powder (γ-Al₂O₃, PURALOX HP-14/150, Sasol Germany GmbH) was impregnated with the metal/metals using the incipient wetness technique. The bimetallic catalysts were prepared by co-impregnation of the two metals, by mixing solutions of palladium and platinum nitrate. The support was impregnated twice, with a drying step at 300 °C for 4 h in between, and calcined at 1000 °C for 1 h. All catalysts had a loading of 470 μmol metal/g catalyst powder. The details regarding these catalysts are summarized in Table 1.

The catalyst powders were suspended in ethanol and ball-milled for 24 h prior to coating the monoliths. Cordierite monoliths (400 cpsi, Corning), with φ 14 mm and length 10 mm, were then dipped into the slurry followed by a drying step at 100 °C. This procedure was repeated until 20 wt.% of catalyst material was fastened onto the monolith. Finally, the coated monoliths were calcined at 1000 °C for 2 h.

2.2. Characterization

Inductive coupled plasma-atomic emission spectroscopy (ICP-AES) was performed on all catalyst powders in order to verify the amounts of palladium and platinum.

The specific surface areas of the catalyst powders were measured according to the Brunauer–Emmett–Teller (BET) theory by nitrogen adsorption at the liquid N₂ temperature in a Micromeritics ASAP 2010 instrument. Prior to analysis, the samples were degassed for at least 2 h at 250 °C.

The CO-chemisorption measurements were performed on the catalyst powder by using a volumetric technique. Prior to the measurements, the samples were dried in vacuum at 120 °C, reduced in a flow of H₂ at 300 °C for 1 h, evacuated at 300 °C for 1 h and then cooled to 35 °C. The CO-chemisorption analyses were thereafter carried out using a dual isotherm method.

The crystal phases in the various catalysts were identified by means of powder X-ray diffraction (PXRD) using a Siemens Diffrakometer D5000. The operation parameters were: Cu Kα radiation, Ni filter, 30 mA, 40 kV, step size 0.02 and 2θ scanning from 20 to 80° at a rate of 1 s per step. The crystal phases of the noble metals were studied more carefully in between 32 and 44°, by a step size of 0.01 at a rate of 8 s per step. Phase identification was done using the reference JCPD database and the mean crystal size estimation was done using the Fundamental Parameter Approach application of the TOPAS v2.0 software.

The DRIFTS spectra were recorded using a Nexus 870 FTIR instrument equipped with a diffuse reflectance accessory that includes a reaction cell. The catalyst powder was placed inside the reaction cell, in which the temperature and atmosphere were controlled. The spectrometer collected 42 spectra in the range of 2000–4000 cm⁻¹, with a resolution of 16 cm⁻¹ at a mirror velocity of 1.89 cm s⁻¹.

A typical run consisted of several steps. In order to remove absorbates from the catalyst surface, the powders were pretreated in 4% O₂/He flowing at 35 ml/min; the temperature was elevated to 320 °C and kept constant for 1 h. After cooling to the desirable reaction temperature, a background was collected using the parameters for the spectra collection described above. Thereafter, the programmed collection of series of spectra started simultaneously with a gas tank mixture of 1% CH₄, 4% O₂, balance He being switched on. It was added to the feed into the reaction cell. The collection lasted for 50 min, while the temperature was kept constant. In order to study the desorption of species, the methane flow was turned off after 30 min.

2.3. Activity measurements

The measurements of the catalytic activity of the different catalysts were carried out in a tubular reactor, equipped with a temperature-programmed furnace. The temperature was recorded in the gas phase by a thermocouple placed upstream of the monolith. The gas compositions used in the experiments consisted of 1.5 vol.% fuel in air, where the fuel was methane in most cases, but also hydrogen and ethane have been tested.

The first experiment was carried out at a gas hourly space velocity of 250 000 h⁻¹. For this experiment the composition of the product gas was analyzed by gas chromatography, using a Varian 3800 instrument equipped with a thermal detector. The activity of methane combustion was measured for 12 h, when the temperature was maintained at 500 °C.

The following activity tests were carried out at a gas hourly space velocity of 100 000 h⁻¹ and the composition of the

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Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pd/Al₂O₃</th>
<th>2:1PdPt/Al₂O₃</th>
<th>1:1PdPt/Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>5 wt.% Pd/Al₂O₃</td>
<td>2:1 Pd/Pt/Al₂O₃</td>
<td>1:1 Pd/Pt/Al₂O₃</td>
</tr>
<tr>
<td>Pd loading (wt. %)</td>
<td>5.01</td>
<td>3.3</td>
<td>2.6</td>
</tr>
<tr>
<td>Pt loading (wt. %)</td>
<td>–</td>
<td>3.0</td>
<td>4.7</td>
</tr>
<tr>
<td>BET surface area (m²/g)</td>
<td>102</td>
<td>91</td>
<td>107</td>
</tr>
<tr>
<td>CO-uptake (μmol/g catalyst)</td>
<td>7.3</td>
<td>5.2</td>
<td>7.0</td>
</tr>
<tr>
<td>Crystal size PdO (nm)</td>
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<td>22</td>
<td>23</td>
</tr>
<tr>
<td>Crystal size Pd–Pt (nm)</td>
<td>–</td>
<td>47</td>
<td>36</td>
</tr>
</tbody>
</table>
product stream was analyzed by paramagnetic and IR-spectroscopy techniques. A range of tests when extra water vapor was added to the feed were performed while measuring the methane conversion. Water vapor was added to the feed stream by means of a syringe pump and evaporator in the concentrations of 1.25, 2.5, 5 and 10 vol.%. The regeneration of the Pd/Al₂O₃ was tested by purging the catalysts in nitrogen or air. The activity of combustion of H₂ and C₂H₆ were also measured over the Pd/Al₂O₃ catalyst for 5 h, in order to study the stability of conversion.

3. Results and discussion

3.1. Catalyst materials

The PXRD patterns of the three catalysts after calcination are presented in Fig. 1 for 2θ values between 32 and 44°. In the Pd/Al₂O₃ catalyst, the palladium was found in the form of PdO and only very small amounts of metallic Pd were detected. The opposite was observed for the bimetallic catalysts. Only a small amount of PdO was found in 2:1PdPt/Al₂O₃; the amount was even smaller in 1:1PdPt/Al₂O₃. On the other hand, the reflection of metallic Pd was considerably larger, but the positions of the Pd peaks were shifted to lower 2θ values. Since no other phases of platinum were detected this shift is most likely due to platinum incorporation in the palladium structure, forming a solid solution. From previous TEM/EDS studies, it has been concluded that the particles are divided into two different domains, i.e. PdO and Pd–Pt alloy, which coexist in the Pd–Pt catalysts [21]. This is in agreement with the XRD data presented in this paper. From the PXRD patterns between 20 and 80°, the δ-phase of alumina was identified for all three catalysts.

The textural properties of the catalyst materials are reported in Table 1. The BET surface areas of the catalysts after calcination at 1000 °C vary slightly, as well as the CO-uptake. The crystal sizes determined from PXRD showed that the PdO crystallites were smaller than the alloyed particles.

3.2. Catalytic activity

Typical combustion behaviors for palladium-based catalysts are shown in Fig. 2. The monometallic palladium catalyst, Pd/Al₂O₃, initially has an excellent activity for methane conversion. However, the activity declines severely during the course of the experiment, even though the temperature and the other reaction parameters are kept constant. This behavior of monometallic palladium catalysts has previously been reported in the literature for various temperatures and pressures [7–12].

The activity of the bimetallic catalyst, 2:1PdPt/Al₂O₃, on the other hand, increases slightly with time. The increase is due to the initially Pd-rich solid solution changing composition during operation under lean conditions toward a more stable phase with equal molar amounts of Pd and Pt [23]. At the same time as Pd diffuses out from the solid solution it becomes oxidized, since PdO is the thermally stable phase in the temperature range used in the experiment. A previous report has shown that the Pd–Pt alloy itself has poor activity for methane combustion [21]. Therefore, an increase in the amount of the PdO phase will increase the activity for methane combustion.

Fig. 2 indicates that the 2:1PdPt/Al₂O₃ catalyst is more active than Pd/Al₂O₃ after only 6.6 h. Since the commercial demand on the catalyst in gas turbine combustors is to withstand at least 8000 h [24], the bimetallic Pd–Pt catalyst seems to be a better choice.

In Fig. 3 the results of regeneration of Pd/Al₂O₃ are shown. The methane conversion was measured for 30 min at 500 °C, whereas the catalyst was purged with either nitrogen or air in the absence of methane for another 30 min. This cycle was repeated three times and is denoted 1, 2 and 3 in the figure. For
the first cycle the activity is initially very high and almost reaches full conversion. The methane conversion then drops during the 30 min interval. Thereafter, the catalyst is purged with nitrogen/air at the same temperature; consequently no methane conversion is shown in the figure. When the methane is again turned on the conversion does not reach the same high value as in the beginning of cycle 1. However, it appears that air is slightly better than nitrogen for recovering the activity of Pd/Al2O3. The same trend is shown for the other cycles as well, but the difference between the two purging gases is slightly more pronounced in the subsequent cycles.

In the cycle denoted A in Fig. 3 the catalyst is exposed to a temperature peak above 600 °C due to a quick increase of the concentration of methane in the feed, followed by a purging step in nitrogen. By this treatment, the catalyst actually regains its initial activity, seen by the high activity in the beginning of cycle 1. Hence, it is possible to recover the activity of Pd/Al2O3, but not by purging the catalyst in nitrogen or air at 500 °C. A considerably higher temperature is most likely required for the regeneration.

The fact that it is possible to recover the activity indicates that either the morphology of the particles is changing very fast upon this heat treatment or that something is desorbing from the catalyst surface that has blocked the active sites. It is suggested in the literature that the decrease in activity during operation over supported palladium-based catalysts is due to sintering of the palladium particles [8,25]. According to Lyubovsky and Pfefferle [26] it is possible to redisperse the particles upon heat treatment above the thermal decomposition of PdO; this is therefore a possible explanation to the reactivation of the Pd/Al2O3 catalyst.

The decreasing activity has also been attributed to inhibition by the water generated in the combustion reaction [14–20]. The main reason for the water inhibition has been ascribed to formation of Pd(OH)2, which effectively blocks the active PdO phase. Pd(OH)2 has very low activity for methane conversion and the level of conversion therefore decreases with increasing amount of hydroxyls on the surface. However, the effect of water is less pronounced at higher temperatures and conversions as Pd(OH)2 decomposes into PdO if the temperature is high enough [16], which may occur during cycle A in Fig. 3. The conditions where water inhibition becomes negligible depend both on the oxygen mobility of the support [20,27] and the water concentration [28,29]. Of the commonly used supports alumina has the lowest oxygen mobility [30], resulting in low resistance to water inhibition. Kikuchi et al. [28] have shown affect of water on the methane conversion even for temperature above 600 °C when the water concentration in the feed was 20%.

Since water inhibition could be a possible explanation for the poor stability of Pd-based catalysts, the Pd–Pt catalyst with its higher stability must also be more resistant to water. The following sets of experiments therefore included water vapor in the reaction feed in order to investigate this feature.

3.3. Effect of water vapor on the catalytic activity

The effect of water has been studied over the three catalysts and the results are shown in Figs. 4–6. In Fig. 4 the activity is presented in terms of methane conversion versus time on stream when 5 vol.% water vapor is periodically added to the feed stream. The behavior is clearly different over the monometallic and than that of the bimetallic catalysts when extra water is present in the feed. As previously shown, Pd/Al2O3 gradually loses activity with time, but the difference between the two purging gases is slightly more pronounced in the subsequent cycles.

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findings of Araya et al. [13], that water enhances the deactivation process of Pd catalysts.

The bimetallic catalysts behave differently in presence of water. When water vapor is added to the feed stream the activity decreases abruptly to a lower level, which is kept during the whole water step. When the vapor is removed the activity is wholly recovered to the level before the introduction, suggesting that water does not affect the bimetallic catalysts to the same extent as for Pd/Al₂O₃. It is interesting to note that both bimetallic catalysts have similar behavior when water is present, despite the different PdO concentrations in the catalysts.

The two different types of behavior observed for the monometallic and the bimetallic catalysts indicate that two different deactivation processes occur during water exposure. The stepwise deactivation observed for the bimetallic catalysts indicates that water molecules are weakly adsorbed on the catalyst surface and cover only some of the active sites. This adsorption will most likely be discontinued as soon as the water is removed, as shown in the experiments. This process is also possible to some extent for Pd/Al₂O₃, but this catalyst also experiences another deactivation process since the conversion decreases continuously during the entire water period. The gradually decreasing activity may be due to the slow formation of surface hydroxyls and consequent buildup. When methane is removed from the feed, hydroxyl desorption can be very slow [19,31].

The influence of water concentration on the performance of the catalysts was tested as well, shown in Fig. 5. Again, the behavior differs between the catalysts. After an initial large activity decrease, the Pd/Al₂O₃ catalyst appears not to be affected by further increase in water concentration, while the decrease in methane conversion is more or less the same for all doses. On the other hand, the impact of water concentration on the bimetallic catalysts is significantly larger. The activity over the bimetallic catalysts only decreases slightly for lower doses, but the decrease grows stronger with increasing concentration.

The effect of water for a slightly longer period was also tested, shown in Fig. 6. The methane conversion was measured for 5 h in the presence of 5 vol.% of water vapor. Similar behaviors were observed in the beginning of the water period, as discussed previously. However, after 50 min the activity of 2:1PdPt/Al₂O₃ actually starts to increase slightly, similarly to the combustion profile acquired under dry conditions. When the water flow was turned off the activity returned to the initial level. 1:1PdPt/Al₂O₃ has an almost analogous combustion profile to that of 2:1PdPt/Al₂O₃, but the increase during the water period begins first after 140 min. In addition, the conversion after the water was removed is higher than its initial activity, probably associated with a larger increase of PdO concentration during operation.

Contrary to the bimetallic catalysts, Pd/Al₂O₃ was continuously losing activity during the entire water period; when water was removed the activity did not revert to the initial level. The combustion profiles of the 5 h tests are very similar to the activity tests without addition of extra water to the feed. The only difference is the lower conversion.

The water tests indicate that it is possible that water inhibition is one of the reasons for the poor stability of Pd/Al₂O₃. However, whether surface hydroxyls generated by the combustion reaction constitute the reason for the larger degradation of Pd/Al₂O₃ than of PdPt/Al₂O₃ is difficult to state from these experiments. Water added to the feed stream does not necessary behave in a similar way as the water generated by the reaction.

3.4. In situ DRIFTS studies

From the water tests described above it is difficult to state whether surface hydroxyls cause the various types of behavior. Therefore, in situ DRIFTS studies were performed over
Pd/Al₂O₃ and 2:1PdPt/Al₂O₃ at 200 °C in the presence of a mixture of methane and oxygen. In Fig. 7 the Gram–Schmidt intensity is displayed for the two catalysts. The Gram–Schmidt plot is a graphical representation of series data that shows the relative infrared response change over the course of the experiment, in this case the change of adsorbed species on the catalyst surface. It is obvious that Pd/Al₂O₃ adsorbs significantly more species than 2:1PdPt/Al₂O₃ during reaction, although the molar amount of noble metals is equal for the two catalysts. The amount of adsorbed species accumulated until the methane flow was shut off after 30 min. Thereafter, the total intensity starts to decrease, indicating that some species were gradually desorbed from the catalyst surfaces. Methane and CO₂ quickly desorb, however, the hydroxyl desorption process is slow and was not completed at the end of the experiments.

Fig. 8a and b shows the DRIFTS spectra of Pd/Al₂O₃ during the reactions of methane combustion and desorption, respectively. In Fig. 8a some representative spectra are displayed, which were collected for various time after the methane introduction. At time 0 min the methane was introduced into the oxygen mixture, and therefore no peaks are shown in the spectrum. During the course of the experiment the spectra changed considerably. A broad band covering the region between 2800 and 3700 cm⁻¹ was successively built up, due to water being absorbed on the sample surface [32]. In the same region, peaks of alumina hydroxyls should be located at 3770, 3723 and 3680 cm⁻¹ [20,33]. These alumina peaks are not distinguishable due to their expected much lower intensity compared to the peaks on PdO and these peak widths which obscure their location [20]. At 3016 cm⁻¹ a discrete peak is observed, which according to the literature arises due to gas phase CH₄ [34–36]. The intensity of the peak is slightly increased as the reaction proceeds, indicating that the methane conversion is decreased, which is in line with previous results. Discrete peaks at 3500, 3556, 3697 and 3733 cm⁻¹ are also identified, which were intensified with time. Consistent with Ciuparu et al. [20] these peaks are hydroxyl groups on the metal oxide surface. The peaks at 3733 and 3697 cm⁻¹ are assigned to terminal and bridged isolated OH species, respectively. The terminal species refers to hydroxyl groups that are attached to a single atom. In contrast, bridge OH species refer to hydroxyl groups that are attached to multiple atoms. The peaks at the lower frequencies at 3500 and 3556 cm⁻¹ are ascribed to multiple absorption peaks. Since all the hydroxyl peaks increase simultaneously with the methane peak, it is possible that the surface hydroxyls created by the reaction inhibit the methane conversion. However, one should remember that this experiment was carried out at much lower temperature than in the activity tests described previously. As the formation of hydroxyls may be influenced both by the concentration and the
temperature [16,19,28,29], it is not certain that the surface hydroxyls will be present at 500 °C.

The desorption behaviour of Pd/Al₂O₃ is illustrated in Fig. 8b. The two spectra are very alike, except that the methane peak is absent in the spectrum collected after 50 min. The other peak does not change considerably, but the large band between 2800 and 3700 cm⁻¹ is slightly reduced. Hence, the desorption of water species is very slow, which is in accordance with the results found in the literature [17,19,31]. As the formation of surface hydroxyls is stopped after removal of the methane it is suggested that the hydroxyls arise from the methane reaction.

A comparison of Figs. 8a and b and 9a and b indicates that less steady state concentration of surface hydroxyls are absorbed on 2:1PdPt/Al₂O₃ than on Pd/Al₂O₃. Otherwise the features in spectra are very similar. It is difficult to quantitatively compare the peaks of the two catalysts due to the broad water band. No additional peaks are found in the tested range of wave numbers for 2:1PdPt/Al₂O₃, although the peaks are slightly more distinct. The FTIR bands in Fig. 9a and b likely appear more distinct on the Pd–Pt/Al₂O₃ sample because there are fewer hydroxyls leading to a broad peak, in comparison to the bands in Fig. 8a and b. The methane peak is somewhat decreased during reaction, consistent with an improved activity with time, in line with the activity tests presented in Fig. 2. It is interesting to note that also this catalyst produces surface hydroxyls at 3500, 3556, 3697 and 3733 cm⁻¹, despite the more stable conversion. However, the peaks at 3697 and 3733 cm⁻¹ have lower intensity than those for Pd/Al₂O₃. No separate hydroxyl peaks for either Pt or the alloy could be identified in the range of wave numbers tested, indicating that the hydroxyl species appear to large extent on the PdO domain and less on the alloy. If this is the case, the lower hydroxyl formation on the alloy may result in a cleaner surface that has higher ability to dissociatively absorb CH₄. The rate-determining step for catalytic combustion of methane is often considered to be the cleavage of the first C–H bond [37–39]. According to Burch and Hayes [37] the reason for water inhibition is that this cleavage step becomes even slower if surface hydroxide ions are formed since they are considered to be inactive for activation of the C–H bonds. It has previously been suggested that small amount of metallic Pd enhance the catalytic activity due to the increase in the dissociation rate of the first C–H bond [40], which also may be the case for the alloy. Therefore, the bimetallic catalysts may be less affected by the surface hydroxyl formation as it has other ways of splitting the methane molecule than on PdO due to the alloy.

During the desorption interval, the rate of decrease is similar for both catalysts studied suggesting that desorption mechanism at 200 °C is similar.

### 3.5. Combustion stability of various fuels

Different fuels (H₂, CH₄ and C₂H₆) have been tested in order to investigate if the decrease of conversion over Pd/Al₂O₃ is revealed for fuels other than methane. The choice of fuels was based on their ability to produce water during combustion. The experiments were performed without additional water. As illustrated in Fig. 10, the stability of conversion over Pd/Al₂O₃ is not the same for the various fuels. The conversion of hydrogen was very stable throughout the experiment, even though the reaction product was only water. Ethane on the other hand, worked deactivatingly to some extent, but not as significantly as for methane. These results are inconsistent with the theory of water inhibition by physical modification of the catalyst during operation. Ethane produces more water per combusted molecule than methane; the inhibition should therefore be more pronounced for the ethane conversion. Consequently, water inhibition is most likely not the only factor that determines the stability of conversion.

The splitting of the first bond of the methane molecule is known to be a rate-determining step in the methane combustion.
reaction. Nevertheless, ethane has much weaker C–H bonds than methane, which makes the first bond of ethane easier to break. Hence, the less strong C–H bonds in the ethane molecule may compensate for the deactivation process. That there is a balance between inhibition of the surface by water and the ease of activation of the hydrocarbon has been suggested by Burch et al. [17]. However, their activity was measured at lower temperatures than used in the tests presented in this paper, and it should be keep in mind that the DRIFTS studies only indicate surface hydroxyls up to 200 °C and it is not certain that the surface hydroxyls are present at higher temperatures. Descorne et al. [39] have reported small traces of ethylene during ethane combustion, which indicates that the reaction mechanism is slightly different compared to methane.

When considering the hydrogen conversion, the combustion is faster and occurs at much lower temperature (200 °C) than for the alkanes (500 °C). Hence, the cleavage of the H–H bond is likely fast and is probably not a rate-limiting step to the same extent as in the reaction of the alkanes. It may also appear on different active sites. Therefore, the conversion of hydrogen is able to maintain its level with time, despite the production of water.

4. Conclusions

The following conclusions can be drawn from this work:

- Monometallic palladium catalysts supported on alumina have poor stability for methane conversion. By adding platinum to the catalysts a considerably higher stability is achieved.
- It is possible to regenerate the activity of Pd/Al₂O₃ by a quick temperature rise above 600 °C.
- When additional water vapor is added to the feed stream both Pd/Al₂O₃ and bimetallic Pd–Pt catalysts are affected. However, the ways the catalysts behave are different. The Pd/Al₂O₃ catalyst loses activity at a faster rate than under dry conditions. After the water is removed the activity of this catalyst is not fully recovered to the initial value. The Pd–Pt catalysts, on the other hand, are inhibited by water to a lower degree and the rate is initially fast but levels off quickly. After removal of water, the activity is fully recovered. The degree of activity loss over the bimetallic catalysts is dependent on water concentration in the feed stream.
- DRIFTS studies showed that surface hydroxyls are formed on both types of catalyst during methane combustion at 200 °C. The desorption of this species is slow. The bimetallic Pd–Pt catalyst shows a lower steady state concentration of surface hydroxyls during reaction. As no hydroxyl peak from the alloy or Pt was observed, it might be possible that the alloy domain is less affected by the water present. The alloy domain may therefore help with the splitting of the methane molecule that often is stated to be the rate-limiting step.
- The drop of conversion over Pd/Al₂O₃ is not seen for all fuels that produce water during combustion. Hydrogen presents a very stable conversion over Pd/Al₂O₃. In contrast, the conversion of ethane is slightly decreasing with time, but not to the large extent observed during methane conversion. Hence, the water production during combustion does not likely cause deactivation through physical restructuring of the catalyst. The strength of the bonds in the fuel molecule may also affect the deactivation.

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References
