Catalysts for Methane Total Oxidation

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Abstract

Methane, emitted during the incomplete combustion of natural gas vehicles, is an air pollutant that needs to be controlled. In this work, various catalysts were studied for the total oxidation of methane. Pd, Ni and Pd-Ni deposited on a commercial yttria-stabilized zirconia (YSZ) were synthesized by wet impregnation and calcined at 750°C in air and in N2 to study the influence of the calcination treatment. The six samples were characterized by X-ray diffraction. Their catalytic performances were studied for methane oxidation at 500°C along with five perovskites (LaMnO3, LaMn0.98Pd0.02O3, SrTiO3, SrTi0.98Cu0.10O3, SrTi0.95Mn0.05O3). Pd/YSZ and Pd-Ni/YSZ calcined in air and in N2 showed good activity due to the presence of PdO and it was observed that nickel had a positive synergistic effect on the bimetallic catalyst calcined in air. Stability tests at 350°C for 26h were also conducted for these four samples but it was observed that they weren’t very stable in these conditions.

Keywords: Methane oxidation; Perovskites; Metals; Supported oxide catalysts; Oxygen vacancies.

1. Introduction

Nowadays, one of the major concerns related with the use of fossil fuels is air pollution, global warming and hence climate change that affect natural and human systems. In order to protect air quality and human health, strict regulations for harmful exhaust emissions (NOx, SOx, GHG, PM) [1] have been adopted in the past and will likely be more severe in the future since current limits have not yet reach the effect desired.

One of these air pollutants is methane emitted from natural gas vehicles due to the incomplete combustion of the fuel. Methane is a powerful greenhouse gas, 28 times more effective than carbon dioxide at trapping heat in the atmosphere [2] and it’s more difficult to oxidize than most hydrocarbons due to the lack of C-C bonds. However, the efficiency of methane combustion can be improved by carrying out the reaction in the presence of a catalyst. The catalysts typically used in natural gas fueled vehicles after-treatment generally contain highly active supported precious metals like palladium or platinum. Several studies of methane oxidation over Pd and Pt have been reported [3], [4], [5]. It was found that Pd is more active than Pt for methane oxidation.

Even though methane is the simplest hydrocarbon, the mechanistic pathway of oxidation over noble metals has not been yet clearly identified. Under oxidizing feed-stream conditions, the chemisorption of methane on noble metals involves the dissociation of CH4 into adsorbed methyl or methylene radicals as a result of the removal of hydrogen atoms from the carbon atom. The subsequent interaction of methyl or methylene radicals with the adsorbed oxygen leads to the formation of carbon dioxide and water. The oxidation of CH4 might occur on metallic palladium, on a palladium oxide surface, or even on a surface partially covered with oxygen. Most researches [4] agree that at low temperature (below 700–800°C) methane oxidation involves its reaction with surface PdO species followed by reoxidation of palladium with oxygen. Fujimoto et al. [6] slightly modified this redox mechanism and postulated the presence of oxygen vacancies on the PdO surface and the activation of methane occurs on site pairs consisting of oxygen atoms (surface PdO) and oxygen vacancies (surface Pd).

One of the catalysts that has been extensively studied is Pd supported on Al2O3. Domingos et al. [7] reported that palladium is present in the form of PdO at alumina surface and that measurable conversions were observed at temperatures above 250°C, and the level of 100% conversion was reached around 550°C.

Transition metals based catalysts are also good options for methane combustion. Among them, perovskites oxides (ABO3) are good options due to their low-cost, high thermal stability, redox properties and versatile structures. The catalytic activity of ABO3 is determined primarily by the kind of transition elements at the B-site [8]. Furthermore, A and B cations can be partially substituted by other suitable elements (noble or transition metals), which can result in a profound modification of
the catalytic activities, usually by influencing oxygen availability. This partial substitution causes different oxidation states of the metals as well as non-stoichiometry (commonly anionic vacancies) in order to keep the electroneutrality of the oxide.

The oxidation process on perovskites can be divided into suprafacial and intrafacial mechanisms. The suprafacial process is observed at low temperature and involves adsorbed or surface oxygen, which it’s assumed to react with gaseous methane (Rideal-Eley mechanism). The intrafacial mechanism involves the lattice oxygen as active specie and occurs at higher temperatures, where bulk oxygen has mobility to migrate to the surface and reacts with methane (Mars-van-Krevelen mechanism).

Arai et al. [9] studied methane total combustion over various LaBO$_3$ perovskite (B= Co, Mn, Fe, Cu, Ni and Cr) and compared their activity with Pt/alumina. The activity of Pt/alumina catalyst ($T_{50\%} = 518^\circ C$) was higher than the single-perovskites systems. This is partly as a result of the larger surface area of supported metal catalysts versus those of perovskite-type oxides. Besides this, the activities of LaCoO$_3$, LaFeO$_3$ and LaMnO$_3$ catalysts were close to the platinum supported on alumina with $T_{50\%}$ of 525$^\circ C$, 571$^\circ C$ and 579$^\circ C$, respectively.

This paper studies the catalytic total oxidation of methane. To achieve this purpose, methane oxidation experiments were performed using metal-supported catalysts and perovskite-based catalysts: Pd/YSZ, Ni/YSZ, Pd-Ni/YSZ, LaMnO$_3$, LaMn$_{0.86}$Pd$_{0.02}$O$_3$, SrTiO$_3$, SrTi$_{0.95}$Cu$_{0.1}$O$_3$ and SrTi$_{0.95}$Mn$_{0.05}$O$_3$.

2. Experimental
2.1. Catalysts preparation and characterization

The catalysts support used in this work was a commercial yttria-stabilized zirconia (YSZ) from Tosoh (13.3 wt% Y, 16 m$^2$/g).
Pd (1.3 wt%), Ni (1.3 wt%) and Pd–Ni (0.6 wt%–0.65 wt%) supported on YSZ were prepared by wet impregnation at room temperature. Three commercial precursors were used: Pd(NO$_3$)$_2$·2H$_2$O, Pd(NO$_3$)$_2$·H$_2$O and Ni(NO$_3$)$_2$·6H$_2$O from Aldrich.

The catalysts were dried overnight at 100$^\circ C$ after impregnation and then calcined in air or in N$_2$, to study the effect of the calcination atmosphere. The calcination comprised two stages, one at 450$^\circ C$ for 4 hours and another at 750$^\circ C$ for 2 hours with a rate of heating and cooling of 5$^\circ C$/min. The samples were labeled Pd(air), Pd(N$_2$), Ni(air), Ni(N$_2$), Pd-Ni(air), Pd-Ni(N$_2$) according to the metal used and, in parenthesis, the calcination atmosphere applied.

Characterization by X-ray diffraction (XRD) was performed with a Bruker D8 Advance Model A25 diffractometer using CuK$\alpha$ ($\lambda = 0.154184$ nm) radiation over a range of 29 angles from 4$^\circ$ to 80$^\circ$.

The perovskites used were: LaMnO$_3$, LaMn$_{0.98}$Pd$_{0.02}$O$_3$ (1.3 wt% Pd), SrTiO$_3$, SrTi$_{0.95}$Cu$_{0.1}$O$_3$ (4.48 wt% Cu), SrTi$_{0.95}$Mn$_{0.05}$O$_3$ (1.96 wt% Mn) calcined in air with the same temperature profile as the catalysts synthesized.

2.2. Catalytic tests for methane oxidation

The catalytic oxidation of methane was carried out in a quartz U-reactor. A reactant flow of 200 mL/min with 3 vol% of O$_2$ and 0.2 vol% of CH$_4$ in helium was fed to the reactor. It was loaded 50 mg of catalyst + 150 mg of SiC (in order to reduce the heat release during reaction).

The temperature profile used in a cycle of catalytic test consisted of heating the reactor at a rate of 5$^\circ C$/min between 25$^\circ C$ and 500$^\circ C$, where it stayed for two hours and then cooling down at the same rate. The concentration measurement of the products outcoming from the reactor was accomplished using a Thermo Scientific - Nicolet iS50 FT-IR Spectrometer. For the catalysts that showed activity, two more cycles were performed and a stability test at 350$^\circ C$ for 26 hour was also carried out.

3. Results and Discussion
3.1. XRD characterization of the catalysts

The diffraction profiles of the catalysts synthesized are shown in figures 1, 2 and 3 as their XRD patterns after the 26h stability test for methane oxidation. Analyzing the three figures, it can be seen that both fresh and aged catalysts are well crystallized due to the high crystallinity degree of the YSZ, which has a cubic structure in all samples prepared.

Starting with the XRD patterns of the fresh catalysts in Fig. 1, a peak is observed for Pd(air) at 33.9$^\circ$ due to the presence of a PdO phase [7] and for the catalyst calcined in N$_2$ is present a peak for metallic palladium at 40.1$^\circ$ [10]. Both diffraction peaks show low intensity due to the low metal content in the catalysts (1.3 wt%). Since each catalyst presents a different palladium form in its structure, it’s possible to conclude that the calcination atmosphere – air or nitrogen – influences the oxidation state of Pd. The XRD results of the catalysts after the stability test reveal that it was not detected the peak corresponding to PdO at 40.1$^\circ$ for both catalysts. It is also not possible to see the peak corresponding to PdO due to the overlapping with the peaks of SiC although it’s assumed that PdO exists, once it’s stable in the presence of oxygen in these conditions. So, for Pd(N$_2$), during reaction occurred the transformation Pd$^\circ$ $\rightarrow$ PdO.

In Fig. 2, both XRD patterns of the two nickel supported on YSZ catalysts prepared present the main peak corresponding to nickel oxide (NiO) at 42.3$^\circ$ [11] and it wasn’t detected metallic nickel, where the typical diffraction peaks appear around 28=44.4$^\circ$ and 51.7$^\circ$ [12]. Unlike in the previous case, here the calcination atmosphere didn’t affect the structure of the catalysts due to the higher stability of this oxide at the calcination temperature applied, and no decomposition occurred. In the
Fig. 1 – XRD patterns of the fresh catalysts (a) Pd/YSZ cal. in air and (b) Pd/YSZ cal. in N₂ and after the 26h test at 350°C for methane oxidation (c) Pd/YSZ cal. in air + SiC and (d) Pd/YSZ cal. in N₂ + SiC.

Fig. 2 – XRD patterns the fresh catalysts (a) Ni/YSZ cal. in air and (b) Ni/YSZ cal. in N₂.

Fig. 3 – XRD patterns of the fresh catalysts (a) Pd/YSZ cal. in air and (b) Pd/YSZ cal. in N₂ and after the 26h test at 350°C for methane oxidation (c) Pd/YSZ cal. in air + SiC and (d) Pd/YSZ cal. in N₂ + SiC.
former case, the metal used was a noble metal which tends to be more stable in the metallic form at high temperature in an inert atmosphere. Note that in Fig. 2 there aren’t shown the patterns for the catalysts after the 26 hours catalytic test due to the very poor activity of these two catalysts for methane combustion (explained in more detail further ahead).

Fig. 3 shows the XRD patterns of the bimetallic Pd-Ni catalysts prepared. Similarly to Pd/YSZ, the XRD diffractograms of these fresh catalysts show a peak corresponding to PdO for the catalyst calcined in air and a peak of metallic palladium for the catalyst calcined in N2. Again, the calcination atmosphere applied in the thermal treatment influenced the palladium phase present there. It wasn’t detected any nickel species (neither NiO or NiO)_2 due to its low concentration (0.65 wt%) and likely good dispersion. It is believed that, as for the Ni/YSZ catalysts, the NiO phase is present in both catalysts. In the XRD patterns of the catalysts after the 26th stability test: nickel was not detected again; the presence of a PdO peak it’s not clear due to the overlapping with one of the peaks of SiC, although it’s believe that this phase exists for both catalysts; and PdO peak disappeared for Pd-Ni(N2) so, during reaction the oxidation of Pd to PdO occurred in the catalyst calcined in nitrogen.

Based on the metal phases detected on the XRD profiles shown in Fig. 1, 2 and 3, the crystallite size of PdO, PdO and NiO present in the different catalysts was estimated from their main peak by the Scherrer equation [13]. The values obtained are listed in Table 1.

### Table 1 – Average crystallite size of the metal phases detected in the XRD profiles.

<table>
<thead>
<tr>
<th>Fresh Catalyst</th>
<th>Metal phase</th>
<th>Average particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/YSZ (air)</td>
<td>PdO</td>
<td>15</td>
</tr>
<tr>
<td>Pd/YSZ (N2)</td>
<td>PdO</td>
<td>44</td>
</tr>
<tr>
<td>Ni/YSZ (air)</td>
<td>NiO</td>
<td>42</td>
</tr>
<tr>
<td>Ni/YSZ (N2)</td>
<td>NiO</td>
<td>39</td>
</tr>
<tr>
<td>Pd-Ni/YSZ (air)</td>
<td>PdO</td>
<td>25</td>
</tr>
<tr>
<td>Pd-Ni/YSZ (N2)</td>
<td>PdO</td>
<td>73</td>
</tr>
</tbody>
</table>

From table 1 it can be seen that regarding the two Ni/YSZ catalysts synthesized, the nickel oxide phase presents similar particle size (42 and 39 nm) showing again that the calcination atmosphere didn’t influence the metal phase present in the catalysts. Comparing the two Pd/YSZ catalysts, the particle size of PdO is larger than the particle size of PdO (44 against 15 nm, respectively). This is also confirmed in the PdO and PdO particle size of the Pd-Ni based catalysts (73 against 25 nm, respectively) although in these two catalysts the values measured are higher than for the Pd/YSZ showing that nickel addition to the catalysts influences the catalyst structure increasing either PdO or PdO particle size. The formation of larger PdO/PdO crystallites in the bimetallic catalysts is due to the competition between palladium and nickel nitrate precursors for the support sites during the preparation step. The interaction of both metals with the YSZ support occurs simultaneously thus, less surface is available for each metal on the support and, consequently, larger particles are formed in comparison with the monometallic catalysts.

3.2. Catalytic activity for methane oxidation

Fig. 4A, B, C and D present methane conversion profiles obtained in the catalytic tests for Pd(air), Pd(N2), Pd-Ni(air) and Pd-Ni(N2), respectively. These four catalysts showed good activity and the selectivity of CO2 was 98-99% for all four catalysts. Methane conversion starts at about 250°C for the catalysts calcined in air and around 300°C for the samples calcined in nitrogen. Among these four catalysts, Pd(air) is the sample that shows the highest activity. The catalytic activity of these catalysts follows the trend (T95% (°C) in parentheses): Pd(air) (364) > Pd(N2) (375) > Pd-Ni(air) (407) > Pd-Ni(N2) (455).

The perovskites SrTiO3, SrTi0.95Cu0.05O3 and SrTi0.95Mn0.05O3 didn’t show any activity towards methane oxidation in these conditions and the following catalysts showed very poor activity, with the maximum conversion obtained at 500°C in parenthesis: LaMn0.98Pd0.02O3 (26%), LaMnO3 (15%), Ni(air) (6%) and Ni(N2) (4%).

Analyzing Fig. 4A and 4B, regarding the two Pd/YSZ catalysts, both catalysts show high activity for methane oxidation. For Pd(air) the maximum methane conversion obtained was 94%, achieved during the first catalytic cycle, at about 500°C. Pd(N2) obtained a maximum conversion of 93% but this value was only attained during the 2nd cycle of reaction, which means that some structural transformations occurred in the catalyst during the 1st cycle of reaction. Taking into account the XRD results, where in the fresh sample was only observed metallic Pd, while in the aged catalyst this specie was not detected, means that the initial lower methane conversion attained in the 1st cycle is due to the lower activity of the catalyst when Pd is present in the metallic state. The Pd/PdO transformation and the consequent change in the surface reactivity is a relevant characteristic of these palladium supported catalysts. With this information is possible to conclude that reduced Pd is inactive or less active for methane combustion compared with the oxide form. The same behavior is verified in Fig. 4C and 4D, where the maximum conversion obtained for the bimetallic catalysts increased in each cycle of reaction, not only for the Pd-Ni(N2), where again the PdO present in the fresh catalyst was oxidized to PdO during reaction, but also for the Pd-Ni(air), which means that structural changes could also have occurred in the PdO particles, probably sintering of the particles that could lead to a more favorable structure of PdO, allowing a more rapid and efficient dissociative oxygen adsorption increasing the catalyst activity [14]. Nickel (in the form of NiO based on the XRD of Fig. 2) also influenced the
catalysts performance, at least Pd-Ni(air). Since both Ni/YSZ catalysts alone show almost none activity in these conditions and the amount of palladium in the bimetallic catalysts (0.6 wt%) is more or less half the quantity present in the Pd/YSZ samples (1.3 wt%), it should be expected that the conversion obtained in the Pd-Ni catalysts should be half of the conversion obtained for the Pd-catalysts at the same temperature, when in a kinetic control regime. However, at 400°C for example, the conversion obtained for the 3rd cycle of reaction was 72% for Pd(air) and for Pd-Ni(air) was 46%, more than a half of the conversion obtained for the palladium based catalyst alone, so it is possible to conclude that nickel has a promotional effect in this bimetallic system, enhancing the catalytic activity of the catalyst. This type of effect has already been reported in the literature [15][16]. In the case of Pd(N₂) and Pd-Ni(N₂) that wasn’t verified at 400°C, where the conversion attained was 67% and 24%, respectively. One possible explanation for the influence of Ni as a second metal on the Pd catalyst performance is that the addition of nickel modifies the electronic state of palladium leaving it more electron-deficient, which makes it easier to bond with oxygen atoms from the atmosphere [16],[17]. The positive synergetic effect of Ni over Pd presents the advantage of synthesis of catalysts with low Pd loading, which is expensive, and use a less expensive metal like nickel.

Besides the effect of the calcination atmosphere, the enhanced catalytic activity of Pd(air) regarding Pd(N₂) and of Pd-Ni(air) regarding Pd-Ni(N₂) can be possible related with the palladium particles size: smaller particles exhibit a higher tendency to be oxidized [4],[18] and based on table 1, the palladium particles of the catalysts calcined in air are smaller than the respective particles of the catalysts calcined in N₂.

In Fig. 4A and 4B can be seen the hysteresis phenomena between the heating and cooling steps of the 3rd cycle of reaction. Hysteresis in palladium based catalysts for methane oxidation can be explained by the PdO→Pd transformation: in this temperature range, PdO decomposition can occur during the heating cycle leading to the appearance of some metallic palladium,
less active for methane combustion. When the temperature starts to decrease the Pd⁰ species formed reoxidize increasing the activity of the catalyst and increasing methane conversion for a given temperature when compared with the heating branch [19], [20].

In Fig. 5 is present the results obtained for the 26h stability test at 350°C. It can be observed that Pd(air) and Pd(N₂) needed a high stabilization time in these reaction conditions and it didn’t occur any deactivation during the time of the test. Once PdO is thermodynamic favorable at this temperature, methane conversion increase with time on stream observed in Fig. 5 can be due to a solid-state reconstruction of the PdO particles. It has been reported that a sintering phenomenon of PdO on the surface of the support is observed, which can lead to a more active configuration of the palladium oxide particles for methane combustion allowing a more easy and rapid replenishment of the external oxygen layer that is continuously consumed by the CH₄ molecule [14]. In the case of Pd-Ni(air) and Pd-Ni(N₂), both exhibited low conversion at 350°C, especially Pd-Ni calcined in N₂, which means the amount of CO₂ formed in methane oxidation when Pd-Ni(N₂) is used is very low, and therefore the error in its quantification is much higher (in percentage), which can explain the oscillations that appear in the Time–Conversion plot. It also can be seen that methane conversion slightly increases during the stabilization test, so this catalyst is not stable. In the case of Pd-Ni(air), this catalyst didn’t reach any stable state during the 26 hour experiment so it is not stable in these conditions. It is also possible to say that the addition of Ni affected the stabilization of the bimetallic catalysts when compared with the monometallic Pd-catalysts, influencing the stabilization of palladium particles in the reaction atmosphere, once the conversion trends between the Pd-catalysts and the Pd-Ni catalysts are different.

![Fig. 5](image-url) Methane conversion over Pd/YSZ and Pd-Ni/YSZ calcined in air and in N₂ in a 26 hours stability test at 350°C.

4. Conclusions

From the study of methane total catalytic oxidation the following conclusions can be drawn:

- The calcination atmosphere influenced the palladium phase present at the catalysts surface: for the samples calcined in air, PdO was the stable phase and for the samples calcined in N₂, Pd⁰ was the only species detected. However, it didn’t affect the nickel based catalysts, in which the metal was present in the form of NiO.
- The calcination atmosphere did not affect NiO average particle size. On the contrary, Pd⁰ particles are larger than PdO particles and their size is bigger in the bimetallic systems.
- The catalytic activity of the catalysts studied follows the trend (T₅₀₃(K) in parentheses): Pd(air) (364) > Pd(N₂) (375) > Pd-Ni(air) (407) > Pd-Ni(N₂) (455).
- Nickel revealed a positive synergistic effect in the Pd-Ni(air) catalyst.
- LaMnO₃, LaMn₀.₉₈Pd₀.₀₂O₃, Ni(air) and Ni(N₂) showed poor activity and the perovskites SrTiO₃, SrTi₀.₉₇Cu₀.₀₃O₃ and SrTi₀.₉₅Mn₀.₀₅O₃ didn’t show any activity at all.

References:


