Abstract: In the following work, the catalytic behavior of Pd catalysts prepared using different oxides as support (Al₂O₃, CeO₂ and TiO₂) in the catalytic combustion of propene, in low concentration in excess of oxygen, to mimic the conditions of catalytic decomposition of a volatile organic compound of hydrocarbon-type is reported. In addition, the influence of different promoters (Ce, Ti, Fe and Mn) when added to a Pd/Al₂O₃ catalyst was analyzed. Catalysts were prepared by the impregnation method and were characterized by ICP-OES, N₂ adsorption, temperature-programmed reduction, temperature-programmed oxidation, X-ray diffraction, X-ray photoelectron spectroscopy and transmission electron microscopy. Catalyst prepared using CeO₂ as the support was less easily reducible, due to the stabilization effect of CeO₂ over the palladium oxides. Small PdO particles and, therefore, high Pd dispersion were observed for all of the catalysts, as confirmed by XRD and TEM. The addition of Ce to the Pd/Al₂O₃ catalysts increased the metal-support interaction and the formation of highly-dispersed Pd species. The addition of Ce and Fe improved the catalytic behavior of the Pd/Al₂O₃ catalyst;
however, the addition of Mn and Ti decreased the catalytic activity in the propene oxidation. Pd/TiO$_2$ showed the highest catalytic activity, probably due to the high capacity of this catalyst to reoxidize Pd into PdO, as has been found in the temperature-programmed oxidation (TPO) experiments.

**Keywords:** Pd-doped supported catalysts; CeO$_2$; TiO$_2$; Al$_2$O$_3$ and M/Al$_2$O$_3$ oxides; propene oxidation

1. **Introduction**

One of the major challenges of today is the environmental problem associated with the atmospheric emissions of pollutants after the combustion of fossil fuels. In this way, volatile organic compounds (VOCs) represent a serious environmental problem, because of their direct (carcinogenic or mutagen) and indirect effects (ozone and smog precursors) on the environment and health [1–3]. Several different compounds are usually included in the VOC group, such as aromatic and aliphatic hydrocarbons, alcohols, ketones and aldehydes; compounds that share ease in being oxidized. Therefore, catalytic oxidation of VOCs is an interesting technique in order to reduce the emissions of pollutants during the fossil fuel combustion process, as the low concentration of VOCs in most of the cases does not allow direct combustion [4–6]. Propene is among the most investigated probe molecules in the field of VOC catalytic oxidation, because alkenes are among the major families in automotive exhausts and because of its high photochemical ozone creativity potential (POCP) [7].

Noble metals are often selected as the active phase in most of the VOC catalytic oxidation studies, despite its high price, low thermal stability and tendency of poisoning due to the superior catalytic activity of these species compared to non-noble metals [8]. Most of the catalysts employed in the catalytic oxidation of VOCs are based on the noble metal system, but the development of fuels with a lower quantity of lead, one of the major poisons in palladium catalytic systems [9], has also increased the interest in using Pd as the active phase, due to its lower price compared to other noble metals [10] and its high catalytic activity.

One of the key parameters when developing a catalyst is the nature of the support, as it is well-known that it plays an important role in improving the activity and durability of supported noble metals, with great importance of the surface properties and the metal-support interaction. The catalytic behavior of Pd-supported catalysts in catalytic oxidation strongly depends on the acid-base properties of the support [11,12], as well as on the metal-support interaction [13,14]. The metal-support interaction plays an important role in the oxidation state of Pd during the oxidation of VOCs, as reducible oxides, like TiO$_2$, CeO$_2$, Nb$_2$O$_5$ and La$_2$O$_3$, favor the oxidation of Pd into PdO, while non-reducible oxides do not [15,16]. Pd/Al$_2$O$_3$ catalyst has been studied in the combustion of hydrocarbons by several authors [17–20], showing high catalytic activity despite having different catalytic behavior depending on the hydrocarbon [18]. The addition of reducible oxides (CeO$_2$, TiO$_2$, etc.) can modify the reduction behavior of the catalyst, so it is interesting to check the influence of these oxides in the oxidation state of Pd and, therefore, in the catalytic activity of the system Pd/Al$_2$O$_3$. 
In the present study, the catalytic oxidation of propene was investigated over Pd catalysts supported over CeO$_2$, TiO$_2$, Al$_2$O$_3$ and $M$/Al$_2$O$_3$ oxides ($M=$ Ce, Ti, Fe, Mn). The experimental conditions for the catalytic tests, low concentration of propene (1,000 ppm) in excess of oxygen 9 vol%, were chosen to mimic the conditions of catalytic decomposition of a volatile organic compound of the hydrocarbon-type [2].

The synthesized catalysts were characterized by ICP-OES (inductively-coupled plasma optical emission spectroscopy), specific surface area measurements through the BET method, TPR (temperature-programmed reduction), TPO (temperature-programmed oxidation), XRD (X-ray diffraction), XPS (X-ray photoelectron spectroscopy) and TEM (transmission electron microscopy), in order to evaluate the influence of the different supports and the metal doped on the catalytic properties. Attention was also focused on the catalyst stability during three consecutive cycles.

2. Results and Discussion

2.1. Support and Catalysts Characterization

The physicochemical properties of the commercial supports, Al$_2$O$_3$, TiO$_2$ and CeO$_2$, and doped-Al$_2$O$_3$ supports are listed in Table 1. N$_2$ adsorption-desorption isotherms, pore size distributions and pore volumes of the commercial supports, Al$_2$O$_3$, TiO$_2$ and CeO$_2$, are presented in Figure 1. All commercial supports present a N$_2$ adsorption/desorption profile (Figure 1a) that can be assigned to the Type IV isotherm, showing a hysteresis loop due to capillary condensation representative of a mesoporous material. The three commercial supports, TiO$_2$, CeO$_2$ and Al$_2$O$_3$, of a mesoporous nature, had BET surface areas ranging from ~80–160 m$^2$.g$^{-1}$ and total pore volumes equal to 0.3, 0.4 and 0.2 cm$^3$.g$^{-1}$, respectively. The pore size distribution (Figure 1b) showed a narrow peak centered at 4.6 nm for the Al$_2$O$_3$; a broader peak distribution centered at 8.1 nm was observed for TiO$_2$, while a very low and large distribution curve ranging from around 15 to 50 nm was found for the CeO$_2$ support. After doping of alumina support (5 mol% of Ce, Ti, Fe and Mn) and calcining at 500 °C, the shape of the N$_2$ isotherms remained almost the same as that of the commercial alumina (not shown). The values of BET surface areas associated with the doped-alumina (Table 1) were generally lower than the commercial one, except for Ti/Al$_2$O$_3$, showing almost the same BET surface area as alumina. It is likely that a partial blockage of the pores of the material occurs upon deposition of the metal precursor and calcination at 500 °C 3 h. Accordingly, the mean pore diameter shifted to slightly higher values, suggesting filling of the small pores. However, the total pore volumes being constant at 0.2 cm$^3$.g$^{-1}$, it could be speculated that the metal doping was largely on the external surface of the alumina.

After the Pd introduction, the shape of the N$_2$ isotherms remained almost the same as those of the supports (not shown); however, the specific surface area values were lower (Table 2). This finding could suggest a partial blockage of the porous structure of materials upon Pd deposition and further calcination at 400 °C 4 h. The thermal stability of the doped-alumina supports and Pd catalysts was studied after three tests of propene oxidation (APT: after propene tests), see Tables 1 and 2). The specific surface of the doped-alumina and the Pd catalysts slightly decreased (~10 m$^2$.g$^{-1}$), which means that the properties of both doped-alumina and Pd catalysts were not seriously modified after the heat treatment [21].
Table 1. Physicochemical properties of the supports.

<table>
<thead>
<tr>
<th>Supports</th>
<th>BET surface area (m²·g⁻¹)</th>
<th>BET surface area APT¹ (m²·g⁻¹)</th>
<th>Total pore volume (cm³·g⁻¹)</th>
<th>Mean pore diameter (nm) ²</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>115</td>
<td>-</td>
<td>0.3</td>
<td>8.1</td>
</tr>
<tr>
<td>CeO₂</td>
<td>79</td>
<td>-</td>
<td>0.4</td>
<td>15.0–50.0 (broad curve)</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>157</td>
<td>-</td>
<td>0.2</td>
<td>4.6</td>
</tr>
<tr>
<td>Ce/Al₂O₃</td>
<td>140</td>
<td>128</td>
<td>0.2</td>
<td>5.0</td>
</tr>
<tr>
<td>Ti/Al₂O₃</td>
<td>155</td>
<td>150</td>
<td>0.2</td>
<td>4.5</td>
</tr>
<tr>
<td>Fe/Al₂O₃</td>
<td>145</td>
<td>143</td>
<td>0.2</td>
<td>5.0</td>
</tr>
<tr>
<td>Mn/Al₂O₃</td>
<td>146</td>
<td>145</td>
<td>0.2</td>
<td>5.0</td>
</tr>
</tbody>
</table>

¹ Used after propene tests (APT). ² Calculated by the BJH method.

Figure 1. (a) N₂ adsorption/desorption isotherms and (b) pore size distributions associated with CeO₂, Al₂O₃ and TiO₂ supports.

Table 2. Physicochemical properties of the Pd supported catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>BET surface area (m²·g⁻¹)</th>
<th>BET surface area APT¹ (m²·g⁻¹)</th>
<th>Pd loading (wt%) ²</th>
<th>dCeO₂ (nm) ³</th>
<th>p-Value ⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/TiO₂</td>
<td>102</td>
<td>99</td>
<td>0.8</td>
<td>-</td>
<td>0.64</td>
</tr>
<tr>
<td>Pd/CeO₂</td>
<td>77</td>
<td>77</td>
<td>0.5</td>
<td>105</td>
<td>0.86</td>
</tr>
<tr>
<td>Pd/Al₂O₃</td>
<td>148</td>
<td>144</td>
<td>0.8</td>
<td>-</td>
<td>1.04</td>
</tr>
<tr>
<td>Pd/Ce/Al₂O₃</td>
<td>137</td>
<td>132</td>
<td>0.8</td>
<td>13</td>
<td>-</td>
</tr>
<tr>
<td>Pd/Ti/Al₂O₃</td>
<td>154</td>
<td>142</td>
<td>0.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pd/Fe/Al₂O₃</td>
<td>138</td>
<td>130</td>
<td>0.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pd/Mn/Al₂O₃</td>
<td>135</td>
<td>138</td>
<td>0.8</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

¹ Used after propene tests (APT). ² Pd (wt%) analytical loading determined by ICP-OES. ³ Average CeO₂ crystal sizes determined by XRD for the half-width of the main CeO₂ peaks corresponding to the (111) reflection. ⁴ The ratio between the area of the PdO decomposition peaks and the area of the reoxidation peaks, temperature-programmed oxidation (TPO) analysis.
The results obtained in the X-ray diffraction experiments are plotted in Figure 2. The main diffraction peaks corresponding to the support can be observed for the Pd/Al₂O₃, Pd/TiO₂ and Pd/CeO₂ catalysts (Figure 2a), while peaks corresponding to PdO were only obtained for the Pd/Al₂O₃ catalyst, with a small and broad peak obtained at a 2θ value of 33.9°, which corresponds to the diffraction peak of Miller indices (101). The peaks obtained for the supports correspond to the main diffraction peaks of γ-Al₂O₃, the main diffraction peaks of TiO₂ (brookite) and the typical diffraction peaks related to the cubic lattice of pure CeO₂ (CaF₂ structural type) [22], for the Pd/Al₂O₃, Pd/TiO₂ and Pd/CeO₂ catalysts, respectively. Comparing diffraction profiles obtained for the promoted Al₂O₃-supported catalysts, the main diffraction peaks are due to the γ-Al₂O₃ phase. Only Pd/Ce/Al₂O₃ and Pd/Fe/Al₂O₃ showed diffraction peaks attributed to CeO₂ and Fe₂O₃ phases, with higher intensity of ceria features suggesting higher crystallinity. The presence of the main diffraction peak corresponding to PdO can be observed in Pd/Ti/Al₂O₃ and Pd/Mn/Al₂O₃, while for the other two catalysts, it is not very clear, probably due to the overlap of other diffraction peaks and/or the high dispersion of the PdO particles in these catalysts. It should be remarked that the main diffraction peak of PdO, when present, was very small and broad, which indicates a high dispersion of this metal for all of the catalysts. Moreover, in order to better understand the differences in the catalytic behavior of Pd/CeO₂ and Pd/Ce/Al₂O₃, the crystal size of CeO₂ was determined in these two catalysts by using the Debye–Scherrer equation, using the data from the XRD patterns ((111) reflection of CeO₂). The data obtained are shown in Table 2, where a much lower value of CeO₂ crystal size was found for the catalyst Pd/Ce/Al₂O₃ (13 nm ± 1.3) compared to that obtained for Pd/CeO₂ (105 nm ± 10.5).

**Figure 2.** XRD profiles of (a) Pd-supported catalysts and (b) Pd-doped-supported catalysts, where § denotes reflection of PdO, * denotes reflection of γ-Al₂O₃, + denotes reflection of CeO₂, ^ denotes reflection of TiO₂ and º denotes reflection of Fe₂O₃.

In order to investigate the behavior of Pd-supported catalysts under oxidative conditions, TPO heating/cooling ramps were carried out (Figure 3). During the heating ramp, a positive peak at around 450 °C was observed for Pd/TiO₂ and for Pd/CeO₂ that could be attributed to the decomposition of adsorption oxygen species [23], whereas the positive peak in the range of 750–850 °C could be ascribed to the PdO decomposition [23–25]. The obtained results showed that the PdO decomposition
occurred over CeO$_2$ at higher temperatures than over TiO$_2$ and Al$_2$O$_3$, suggesting for Pd/CeO$_2$ the strongest interaction between the PdO species and the support [24,25]. During the cooling ramp, a single negative peak at 558, 637 and 720 °C, corresponding to the O$_2$-consumption, was observed for the Pd/Al$_2$O$_3$, Pd/TiO$_2$ and Pd/CeO$_2$ catalysts, respectively. This negative peak corresponds to the reoxidation of metallic Pd to PdO [23], and the temperature strongly depends on the support. The finding of such a high reoxidation temperature, 720 °C, for Pd/CeO$_2$ suggests a very high reoxidation tendency of metallic palladium to PdO over ceria. Taking into account the ratio between the area of the PdO decomposition peak and the area of the reoxidation peak, the $p$-value was calculated [24] and reported in Table 2. The smaller the $p$-value, the higher is the reoxidation ability of Pd into PdO. A very low $p$-value was detected for Pd/TiO$_2$.

![Figure 3. TPO profiles of Pd-supported catalysts.](image)

During the cooling ramp, for the Pd/CeO$_2$ catalyst, an oxygen consumption peak occurred also at low temperature, at around 350 °C, which could be associated with the reoxidation of the CeO$_2$ surface partially reduced during the high-temperature heating step.

In Figure 4a, TPR curves of catalysts Pd/CeO$_2$, Pd/TiO$_2$ and Pd/Al$_2$O$_3$, are displayed. Peaks corresponding to different types of PdO species were observed at different temperatures depending on the support. Very small PdO particles (easily reducible, peak at −45 °C) were detected over TiO$_2$. A second peak appearing at 8 °C, also found for Pd/Al$_2$O$_3$, was attributed to the reduction of bulky PdO particles [26]. For both catalysts, Pd/TiO$_2$ and Pd/Al$_2$O$_3$, decomposition of β-hydride species takes place at 60 °C (negative peak). Such species are formed through hydrogen adsorption/diffusion in the Pd° crystallites [27]. Over CeO$_2$, which is known to stabilize PdO, reduction occurred at a higher temperature (25 °C). Moreover, a second peak, at 50 °C, ascribed to the reduction of the ceria surface in contact with palladium, was also found. Above 300 °C, CeO$_2$ and TiO$_2$ were reduced (surface reduction at around 400–500 °C, bulk reduction above 700 °C). Figure 4b, shows the reduction profile of the alumina-doped catalysts. In the Pd/Ti/Al$_2$O$_3$ catalyst, the peak corresponding to the reduction of PdO around 0 °C is much less pronounced than that observed for Pd/TiO$_2$ or Pd/Al$_2$O$_3$, and the decomposition of β-hydride shows two different peaks, probably due to the different interaction of PdH with TiO$_2$ and Al$_2$O$_3$. Pd/Ce/Al$_2$O$_3$ showed two main reduction peaks for PdO at 11 °C and 40 °C,
the first one probably due to the interaction of PdO with Al₂O₃ and the other to the interaction with CeO₂. No clear reduction peak of PdO species was found for the Pd/Fe/Al₂O₃ catalyst, which is probably due to the reduction of this oxide during the stabilization of the signal due to the easiness of this process in this catalyst. Reduction of PdO takes place at 19 °C for the Pd/Mn/Al₂O₃ catalyst, followed by the decomposition of PdH and one big reduction peak at 140 °C, assigned to the reduction of manganese oxides [28].

Figure 4. Temperature-programmed reduction (TPR) curves of (a) Pd-supported catalysts and (b) Pd-doped-supported catalysts.

Figure 5 shows the HR-TEM images of the Pd-supported catalyst and Pd-doped-supported catalysts. All catalysts exhibited small and well-dispersed PdOₓ particles with surface area-weighted PdOₓ diameters between 4–10 nm ± 1.

Figure 5. Cont.
Figure 5. HR-TEM images of the Pd-supported catalysts: (a) Pd/Al\textsubscript{2}O\textsubscript{3}; (b) Pd/Ce/Al\textsubscript{2}O\textsubscript{3}; (c) Pd/Fe/Al\textsubscript{2}O\textsubscript{3}; (d) Pd/Mn/Al\textsubscript{2}O\textsubscript{3}; (e) Pd/Ti/Al\textsubscript{2}O\textsubscript{3}; (f) Pd/TiO\textsubscript{2}; and (g) Pd/CeO\textsubscript{2}.

The chemical state and the chemical surface composition of the Pd-supported catalysts were evaluated by XPS analyses. The binding energies (BEs) and the atomic ratios are presented in Table 3. XPS profiles of the Al 2p for the Pd/Al\textsubscript{2}O\textsubscript{3} and Pd/M/Al\textsubscript{2}O\textsubscript{3} catalysts are shown in Figure 6. The peaks are centered in the range of 74–74.4 eV, for all Al\textsubscript{2}O\textsubscript{3}-catalysts, corresponding to the \(\gamma\)-Al\textsubscript{2}O\textsubscript{3}, in accordance with the XRD results, which mean that the BE of the alumina was not modified after being metal doped. The O/Al atomic ratio showed for the metal-doped catalysts an increased amount of oxygen on the surface. The M/Al atomic ratio changed in the following order: Pd/Ce/Al\textsubscript{2}O\textsubscript{3} < Pd/Mn/Al\textsubscript{2}O\textsubscript{3} < Pd/Ti/Al\textsubscript{2}O\textsubscript{3} < Pd/Fe/Al\textsubscript{2}O\textsubscript{3}; suggesting that among the series of metal-doped catalysts, the highest dispersion on the alumina surface occurred for Fe species.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Binding Energies (eV)</th>
<th>Atomic Surface Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al 2p</td>
<td>(^{1}\text{Pd 3d}_{5/2})</td>
</tr>
<tr>
<td>Pd/TiO\textsubscript{2}</td>
<td>74.1 336.1 (100)</td>
<td>-</td>
</tr>
<tr>
<td>Pd/CeO\textsubscript{2}</td>
<td>74.1 336.4 (100)</td>
<td>-</td>
</tr>
<tr>
<td>Pd/Al\textsubscript{2}O\textsubscript{3}</td>
<td>74.2 336.1 (83.2) 338.1 (16.4)</td>
<td>74.1</td>
</tr>
<tr>
<td>Pd/Ce/Al\textsubscript{2}O\textsubscript{3}</td>
<td>74 336.3 (100)</td>
<td>-</td>
</tr>
<tr>
<td>Pd/Ti/Al\textsubscript{2}O\textsubscript{3}</td>
<td>74 336.1 (100)</td>
<td>-</td>
</tr>
<tr>
<td>Pd/Fe/Al\textsubscript{2}O\textsubscript{3}</td>
<td>74 336.1 (100)</td>
<td>-</td>
</tr>
<tr>
<td>Pd/Mn/Al\textsubscript{2}O\textsubscript{3}</td>
<td>74 336.7 (100)</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^1\) The value in parentheses represents the atomic percentages of the palladium chemical components. \(^2\) The percentages of the chemical states of cerium (\(\text{Ce}^{3+}\) and \(\text{Ce}^{4+}\)) on the surface.
Figure 6. Al 2p XPS spectra of Pd/Al₂O₃ and Pd-doped-Al₂O₃ catalysts.

Figure 7 shows the chemical state of palladium for all catalysts. The Pd 3d spectra of the Pd/Al₂O₃, Pd/M/Al₂O₃ and Pd/TiO₂ catalysts (Figure 7) was characterized by the Pd 3d₃/₂ peak at 336.1 ± 0.6 eV, corresponding to the Pd²⁺ (bulk PdO) [12,29–31], whereas the Pd/CeO₂ catalyst presented the Pd 3d₃/₂ binding energy at 337.4 eV. This peak has been associated by Anna Maria Venezia et al. and Yushui Bi et al. with Pd⁴⁺, as in PdO₂, due to the oxygen incorporation into the PdO crystal lattice during calcinations [12,32].

Moreover, XPS profiles of the Pd/Ce/Al₂O₃ catalyst showed that the oxidized palladium was presented in two chemical states, bulk PdO at 336.1 eV and highly-dispersed and deficiently-coordinated Pd²⁺ in contact with the support to form palladium-aluminate structures at 338.1 eV [31] or PdO₂ [12,32], inducing the formation of new interfacial sites for the oxidation reaction. The percentage of the chemical states of palladium is presented in Table 3. The coexistence of these two oxidation states of palladium and/or the formation of palladium-aluminate structures suggests a greater Pd/Ce/support interaction, as has been described by several authors [31,33]. This Pd-Ce interaction could be promoted by ceria species in the reduced state (Ce³⁺) presented in this catalyst (Table 3) [33]. Moreover, the presence of the Ce³⁺ species results in greater oxygen vacancies due to the formation of a defective ceria structure, as has been reported in previous articles [34]. The increase of the lattice oxygen was related to high metal-particle nucleation sites. Thus, the Ce incorporation on the Pd/M/Al₂O₃-supported catalyst structure favors the formation of highly-dispersed and deficient Pd²⁺, increasing the metal-support interaction and the stabilization of metal particle deposition. Figure 8a shows the Ce 3d spectra of the Pd/CeO₂ and Pd/Ce/Al₂O₃ catalysts, where both catalyst presented the same characteristic peaks of pure CeO₂, according to the convention established by Burroughs [35,36]. Thus, peaks 1, 3, 4, 5 and 6, 8, 9, 10 refer to 3d₃/₂ and 3d₅/₂ binding energies, respectively, and are characteristic of Ce⁴⁺ states, whereas peaks 2 and 7 refer to 3d₃/₂ and 3d₅/₂, respectively, and are attributed to the Ce³⁺ states. Moreover, The Ti 2p spectra of the Pd/TiO₂ and Pd/Ti/Al₂O₃ are shown in Figure 8b. The Ti 2p₃/₂ peak of both catalysts was centered at 458.4–458.5 eV, corresponding to the Ti⁴⁺ species (TiO₂), in accordance with the XRD results. In addition, according to Figure 8c,d, the binding energies of the Fe 2p₃/₂ (710 eV) and Mn-doped 2p₃/₂ (641.9 eV) could be ascribed to the Fe³⁺ (Fe₂O₃) and Mn⁴⁺ (MnO₂) [37,38].
Figure 7. Pd 3d XPS spectra of Pd-supported catalysts.
2.2. Catalytic Tests: Oxidation of Propene

The above characterized catalysts based on Pd supported on Al₂O₃, TiO₂ and CeO₂ were tested in the propene oxidation. The catalytic oxidation of propene was investigated in a tubular fixed-bed reactor under a reactive gas mixture containing 1000 ppm of C₃H₆ and 9 vol% O₂ in He at a gas hourly space velocity (GHSV) of 35,000 h⁻¹. Figure 9 shows the catalytic activity in terms of propene conversion as a function of the temperature (light-off curve) during the cooling ramp. The following sequence in activity was detected: Pd/TiO₂ > Pd/Al₂O₃ > Pd/CeO₂; suggesting that the nature of the support strongly influences the activity.

In order to evaluate the real effect of the support and alumina doping, the catalytic results were expressed as specific reaction rates calculated at 135 °C (mmolC₃H₆ s⁻¹ molPd⁻¹), Figure 10. The same catalytic trend was obtained, where Pd/TiO₂ was the most active, Pd/CeO₂ was the worst sample and Pd alumina-based catalysts showed an intermediate activity. This suggests that the support also plays an important role in the catalytic activity and stability of the Pd catalysts. Thus, the support used has a strong influence on the oxidation state of the active phase, as has been confirmed by XPS. Therefore, the higher catalytic activity of the Pd/TiO₂ and Pd/Al₂O₃ catalysts could be attributed to the Pd²⁺ species detected in these catalysts, while for the case of Pd/CeO₂ catalyst, the presence of Pd⁴⁺ species could be responsible for its low catalytic activity. Moreover, the higher activity of Pd/TiO₂ could be
attributed to the higher ability of this catalyst to reoxidize the metallic Pd into PdO, as has been corroborated by TPO from the parameter \( p \)-value (Table 2), according to the redox properties of this catalyst and the oxygen mobility [12,39].

![Figure 9. C\(_3\)H\(_6\) conversion (%) versus temperature (light-off curve) of (a) Pd-supported catalysts and (b) Pd-doped-supported catalysts, during the cooling ramp.](image)

![Figure 10. Catalytic activity of Pd-supported catalysts as specific reaction rates calculated at 135 °C.](image)

In addition, the obtained results showed that the addition of Ce and Fe improves the catalytic activity of Pd/doped-alumina catalysts, while no positive effect was played by doping of Ti and Mn; Figures 9b and 10. Several factors may contribute to the observed catalytic trend, such as the dispersion of the metal dopant over the alumina, as well as the amount of available oxygen on the catalyst surface. Accordingly, Pd/Fe/Al\(_2\)O\(_3\), exhibiting quite appreciable activity, was characterized by
the highest M/Al surface atomic ratio and quite a high O/Al value. On the other hand, it is likely that other factors influence the activity; indeed, the Pd/Ce/Al₂O₃ catalyst with a very low Ce amount on the surface was the most active Pd-doped-Al₂O₃-supported catalysts. This finding could be attributed to the small CeO₂ crystallites formed in this catalyst and the formation of the highly-dispersed and deficiently-coordinated Pd²⁺ in contact with the support, which favors the higher Pd/Ce/support interaction, as has been observed by XPS and XRD analyses, inducing the formation of new interfacial sites for the oxidation reaction [31].

In other words, the high catalytic activity of the Pd/Ce/Al₂O₃ catalyst could be related to the high Pd/Ce/Al₂O₃ interaction, generated by the increased oxygen vacancy (defects), which promoted the palladium oxide stabilization and more active sites for the oxidation reaction [31,34]. Moreover, Pd/CeO₂ catalyst was less active than the Pd/Ce/Al₂O₃ according to the higher CeO₂ crystallite size and lower surface area [2,31].

In addition, the catalyst stability was evaluated by performing three consecutive catalytic runs for each catalyst. Table 4 lists the temperatures corresponding to 20% (T₂₀), 50% (T₅₀) and 80% (T₈₀) of propene conversion. No appreciable catalytic deactivation was detected after three consecutive catalytic runs, where the different temperatures are close (±10 °C).

Finally, the apparent activation energies were determined for the different Pd-supported catalysts, where the integration equation of first order with respect to propene was used to calculate the reaction rate constants k. The corresponding Arrhenius plots (not shown) were linear for conversion values between 10% and 80%, excluding the occurrence of diffusion limitation. In Table 5, the apparent activation energies Eₐₜ along with the pre-exponential factor A of the Arrhenius equation, \( k = A \ e^{(-E_{act}/RT)} \), are listed. The calculated activation energies and the pre-exponential factors, A, reflect different active site ensembles in the catalysts, as a function of the support.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>T₂₀ (°C) ¹</th>
<th>T₅₀ (°C) ¹</th>
<th>T₈₀ (°C) ¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/TiO₂</td>
<td>136</td>
<td>139</td>
<td>142</td>
</tr>
<tr>
<td>Pd/CeO₂</td>
<td>162</td>
<td>162</td>
<td>166</td>
</tr>
<tr>
<td>Pd/Al₂O₃</td>
<td>149</td>
<td>152</td>
<td>155</td>
</tr>
<tr>
<td>Pd/Ce/Al₂O₃</td>
<td>141</td>
<td>144</td>
<td>148</td>
</tr>
<tr>
<td>Pd/Fe/Al₂O₃</td>
<td>142</td>
<td>145</td>
<td>153</td>
</tr>
<tr>
<td>Pd/Mn/Al₂O₃</td>
<td>153</td>
<td>155</td>
<td>159</td>
</tr>
<tr>
<td>Pd/Ti/Al₂O₃</td>
<td>150</td>
<td>152</td>
<td>158</td>
</tr>
</tbody>
</table>

¹ Light-off temperatures at 20%, 50% and 80% of propene conversion, respectively.
Table 5. Arrhenius parameters \( a \), activation energy \( (E_{\text{act}}) \) and pre-exponential factor \( A \) (s\(^{-1}\)) of the Pd-supported catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>( E_{\text{act}} ) (KJ·mol(^{-1}))</th>
<th>( \ln A )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/CeO(_2)</td>
<td>93.7</td>
<td>26.7</td>
</tr>
<tr>
<td>Pd/Al(_2)O(_3)</td>
<td>132</td>
<td>38.4</td>
</tr>
<tr>
<td>Pd/TiO(_2)</td>
<td>95.3</td>
<td>28.7</td>
</tr>
<tr>
<td>Pd/Ce/Al(_2)O(_3)</td>
<td>162.6</td>
<td>48.1</td>
</tr>
<tr>
<td>Pd/Fe/Al(_2)O(_3)</td>
<td>161.1</td>
<td>47.4</td>
</tr>
<tr>
<td>Pd/Ti/Al(_2)O(_3)</td>
<td>135.1</td>
<td>39.1</td>
</tr>
<tr>
<td>Pd/Mn/Al(_2)O(_3)</td>
<td>130.7</td>
<td>37.6</td>
</tr>
</tbody>
</table>

\( a \) \( E_{\text{act}} \) and \( A \) calculated from the Arrhenius plot in the temperature range 100–170 °C.

3. Experimental Section

3.1. Catalyst Preparation

Commercial oxides, CeO\(_2\) (Aldrich, Milano, Italy), γ-Al\(_2\)O\(_3\) (Aldrich) and TiO\(_2\) (Euro Support Manufacturing B.V., AMERSFOORT, The Netherlands) were used as supports. The doped alumina oxides, M (5 mol%)/Al\(_2\)O\(_3\) (95 mol%), were prepared by wet impregnation of commercial Al\(_2\)O\(_3\) with the corresponding metal (Ce, Fe, Mn) nitrate water solution (Ce(NO\(_3\))\(_3\)·6H\(_2\)O, Fe(NO\(_3\))\(_3\)·H\(_2\)O, Mn(NO\(_3\))\(_2\)·xH\(_2\)O, respectively) or by grafting with Ti(iso-OC\(_3\)H\(_7\))\(_4\), then filtered, dried at 120 °C overnight and calcined at 500 °C for 3 h. Pd catalysts were prepared over the above supports by the impregnation method with Pd(NO\(_3\))\(_2\)·xH\(_2\)O. Then, the obtained powders were calcined at 400 °C for 4 h.

3.2. Catalysts Characterization

The real palladium loading in the catalysts was quantified by ICP-OES Activa (Horiba Jobin-Yvon, Palaiseau, France).

\( \text{N}_2 \) adsorption-desorption at −196 °C was performed on a Sorptomatic 1900 (Carlo Erba, Trezzano sul Naviglio, Italy) instrument. Before the measurement, the samples were degassed at 300 °C for 3 h. The specific surface area (SSA) of each sample was obtained by the Brunauer–Emmett–Teller (BET) method. The mean pore size diameter was calculated by the Brunauer, Emmet, and Teller (BJH) method applied to the desorption curve.

Powder X-ray diffraction (XRD) patterns were recorded on a Bruker (Milano, Italy) D5005 diffractometer equipped with a Cu-K\( \alpha \) radiation (\( \lambda = 1.5418 \) Å) and a graphite monochromator on the diffracted beam, and the XRD data were generally collected in the 2\( \theta \) range of 4°–80° with a scanning step size of 0.02° and 0.5 s. The instrumental broadening was determined by collecting the diffraction pattern of the standard, lanthanum hexaboride, LaB\(_6\). The mean crystallite size (\( d_s \)) of CeO\(_2\) was calculated with a precision of ±10% from the line broadening of the most intense reflections using the Scherrer Equation (1):

\[
d_s = \frac{k \cdot \lambda}{\beta \cdot \cos(\theta)}
\]
where $d_s$ is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size, $k$ (0.9) is the shape factor, $\lambda$ (1.54 Å) is the X-ray wavelength, $\beta$ is the line broadening at half the maximum intensity (FWHM) in radians and $\theta$ is the Bragg angle. A corundum probe (Bruker, Milano, Italy) of known crystallinity has been used as the internal standard.

Temperature-programmed reduction/oxidation (TPR/TPO) experiments were carried out with a Micromeritics Autochem 2910 apparatus equipped with a thermal conductivity detector (TCD). TPR experiments were carried out with a flow rate of 50 mL·min$^{-1}$. The gas mixture with composition 5 vol% H$_2$ in Ar was used to reduce the catalysts (100 mg). Firstly, the sample was cooled down to $-60$ °C in a cold trap, and the TCD signal was registered by gradually increasing the temperature (rate 5 °C/min) from $-60$ °C up to room temperature. After that, the temperature was raised up to 1000 °C at the rate of 10 °C·min$^{-1}$. Before the TPR was started, the catalysts were pretreated with a flowing gas mixture of 5% O$_2$ in He (50 mL·min$^{-1}$) at 120 °C for 1 h in order to purge the surface, then cooling down under Ar. The re-oxidation properties of the catalysts were measured by the TPO experiments. The oxidation gas of 5 vol% O$_2$ in He (50 mL·min$^{-1}$) was used to oxidize the catalysts (100 mg), increasing the temperature from room temperature to 1000 °C at a heating rate of 10 °C/min and then decreasing the temperature from 1000 to 100 °C at a cooling rate of 10 °C·min$^{-1}$.

Chemical states of the atoms in the catalyst surface were investigated by X-ray photoelectron spectroscopy (XPS) on an AXIS Ultra DLD spectrometer marketed by Kratos Analytical, operating with Al (Ka) radiation. XPS data were calibrated using the binding energy of C1s (284.6 eV) as the standard.

High-resolution transmission electron microscopy (HRTEM) analyses were carried out using a JEOL 2100 LaB6 equipped with an Oxford Instruments Inca energy dispersive X-ray (EDX) spectrometer. Mean PdO$_x$ particle size, evaluated as the surface-area weighted diameter ($d_{PdO_x}$), was computed according to the following Equation (2):

$$d_{PdO_x} = \frac{\sum n_i d_i^3}{n_i d_i^2}$$

where $n_i$ represents the number of particles with diameter $d_i$. On average, 50 images for each catalyst have been collected in order to estimate the particle size.

### 3.3. Catalytic Tests

The catalytic activity measurements of the propene oxidation were carried out in a tubular fixed-bed reactor under the reactive gas mixture containing 1000 ppm of C$_3$H$_6$ and 9 vol% O$_2$ in He. The total gas flow rate was 7.2 Lh$^{-1}$ and the amount of catalyst 0.2 g, equivalent to a GHSV of 35,000 h$^{-1}$. In a typical experiment, the fresh catalyst (with grain diameters between 50 and 100 μm) was loaded onto a fine-quartz fritted disk, and the reaction temperature was continuously monitored by a thermocouple inserted inside the furnace. Each catalytic run was performed as follows: introduction of the reaction mixture at room temperature, heating at a rate of 1 °C·min$^{-1}$ up to the final temperature of 450 °C, then cooling down under the reaction mixture. Three consecutive catalytic cycles in propene catalytic oxidation were performed for each catalyst. The total conversion of propene (X) was defined as in Equation (3):
\[ X_{\text{C}_3\text{H}_6}(\%) = 100 \times \frac{[\text{C}_3\text{H}_6]_{\text{in}} - [\text{C}_3\text{H}_6]_{\text{out}}}{[\text{C}_3\text{H}_6]_{\text{in}}} \]  

where \([\text{C}_3\text{H}_6]_{\text{in}}\) and \([\text{C}_3\text{H}_6]_{\text{out}}\) denoted the inlet and outlet concentrations of propene, respectively.

### 3.4. Analysis of Products

The reactants and products of the propene oxidation were analyzed by gas chromatography, using a dual CTR1 column from Alltech (Porapak and molecular sieve) and a TCD for CO, O2 and CO2. A Porapak column and an FID were employed for C3H6 detection. The only reaction products were CO2 and H2O, and the carbon balance was close to ±5% in all of the catalytic tests.

### 4. Conclusions

The catalytic oxidation of propene was investigated over Pd-supported catalysts over CeO2-, TiO2-, Al2O3- and Pd-doped-supported catalysts (M/Al2O3 oxides; \(M = \text{Ce, Ti, Fe, Mn}\)). All catalysts presented well-dispersed PdOx nanoparticles, as confirmed by XRD and TEM. The obtained results showed that the support used has a strong influence on the oxidation state of palladium species and, as a consequence, on the catalytic activity. Pd/TiO2 and Pd/Ce/Al2O3 catalysts were the best performing catalysts, while Pd/CeO2 was performed poorly. Among the series of Pd/doped alumina catalysts, the addition of Ce and Fe improves the catalytic activity with respect to Pd/Al2O3, while no positive effect was played by doping of Ti and Mn. The highest activity of the Pd/TiO2 was attributed to the presence of highly-dispersed Pd^{2+} species easily reducible at −45 °C (as detected by TPR), as well as to the high capability of this catalyst to reoxidize Pd into PdO, as found by TPO. Conversely, in the Pd/CeO2 catalyst, the presence of Pd^{4+} species only, interacting too strongly with the support, seems responsible for its low catalytic activity.

The addition of Ce to the Pd/Al2O3 catalyst increased the Pd-CeO2 interaction, which promoted the palladium oxide stabilization and the formation of more active sites for the oxidation reaction. The presence in the small crystallites of ceria of high oxygen vacancies associated with the presence of Ce^{3+} also contributes to enhancing the oxygen mobility and increasing the catalytic activity of the Pd/Ce/Al2O3, making such a catalyst more active than Pd over bare ceria.

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### Author Contributions

The work was coordinated by Anne Giroir Fendler and Leonarda Francesca Liotta, who contributed equally to the data interpretation and discussion. The manuscript was written by Sonia Gil, who also contributed to the XPS characterization. Mohamed Ousmane performed the synthesis of catalysts and
textural characterization. Giuseppe Pantaleo carried out the TPR and TPO measurements. Jesus Manuel Garcia-Vargas and Laurance Retailleau performed the TEM analyses and catalytic tests.

**Conflicts of Interest**

The authors declare no conflict of interest.

**References**


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