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On the Effect of Preparation Methods of PdCe-MOR Catalysts as NO\textsubscript{x} CH\textsubscript{4}-SCR System for Natural Gas Vehicles Application

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Abstract: In the present work, the effect of several parameters involved in the preparation of PdCe-HMOR catalysts active for NO\textsubscript{x} selective catalytic reduction with methane (NO\textsubscript{x} CH\textsubscript{4}-SCR) was studied. Results show that the catalytic performance of Pd-HMOR is better when palladium is introduced by ion-exchange, namely at room temperature. It was also shown that Pd loading does not influence the formation of cerium species, namely surface Ce\textsuperscript{4+} (CeO\textsubscript{2}) species and CeO\textsubscript{2} species in interaction with Pd. However, when Ce is introduced before Pd, more surface CeO\textsubscript{2} species are stabilized in the support and less CeO\textsubscript{2} become in interaction with Pd, which results in a worse NO\textsubscript{x} CH\textsubscript{4}-SCR catalytic performance.

Keywords: NO\textsubscript{x} HC-SCR; methane; MOR; palladium; cerium; preparation method
1. Introduction

Over the years, efforts have been made by developed countries in order to mitigate air pollution. For instance, in European Union, restrictions to several pollutant emissions have been imposed to each state-member, namely nitrogen oxides (NO$_x$), whose major contribution is due to the road transportation sector.

Depending on the type of engine considered in a vehicle, different after-treatment technologies are available in order to eliminate the NO$_x$ emissions from the engine’s exhaust gases. For instance, when considering positive-ignition engines (typically, for gasoline-powered vehicles), three-way catalysts are able to simultaneously eliminate NO$_x$, CO, and unburned hydrocarbons (HC) in a very efficient way [2]. However, when considering compression-ignition engines (typically, for diesel-powered vehicles), this technology is not effective for NO$_x$ elimination and, thus, other after-treatment need to be considered instead, namely, NO$_x$ storage/reduction systems [3] (also known as lean NO$_x$ traps) and NO$_x$-selective catalytic reduction systems using ammonia (NH$_3$-SCR) [4].

When considering natural gas as a fuel, the most abundant HC in the engine’s exhaust gases is methane and, for this particular type of application, one alternative technology for simultaneous elimination of NO$_x$ and CH$_4$ consists in NO$_x$-selective catalytic reduction using CH$_4$ as a reductant (NO$_x$-CH$_4$-SCR). Metal-containing zeolites have been reported as potential materials to be considered for such application [5–8]. From many different metal/zeolite combinations reported in the literature, PdCe-MOR revealed to be a promising formulation to be considered as NO$_x$-CH$_4$-SCR technology for treating real exhaust gases [9,10]. Notwithstanding, some technological improvements are still required in order to implement this technology commercially.

In order to address some issues regarding the catalytic performance of PdCe-MOR system, it is important to clearly understand the role of the different metal species in the reaction, as well as the parameters that allow controlling the formation/stabilization of such species. In a previous work [11], the optimal loadings of Pd (monometallic formulation) and Ce (bimetallic formulation) were optimized. The purpose of this study is to complement the previously-mentioned work, namely by studying the effect of the preparation method on palladium stabilization in the MOR zeolite, the effect of Pd presence on the stabilization of Ce species, and the effect of metal introduction order.

2. Results and Discussion

2.1. The Effect of Preparation Method on Pd Monometallic Catalysts

2.1.1. Temperature Programmed Reaction under Hydrogen (H$_2$-TPR)

H$_2$-TPR profiles of Pd-HMOR catalysts containing 0.3 wt. % of Pd, introduced by three different methods, are presented in Figure 1.

In all profiles, it is possible to identify a single reduction peak between 70 and 200 °C. According to literature, this peak is attributed to the reduction of Pd$^{2+}$ in exchange position to Pd$^0$ [12–14]. Some authors also refer that the reduction of PdO species might take place at these temperatures [15]. However, the reduction of PdO particles in zeolites is commonly described to occur at ambient or even lower temperatures [12,13,16]. The integration of the peaks (Table 1) shows an H$_2$/Pd ratio similar to
the unity, which is consistent with approximately all Pd in the samples being presented as Pd\textsuperscript{2+} ions in exchange positions.

Figure 1. H\textsubscript{2}-TPR profiles of Pd(0.3)-HMOR catalysts prepared by different methods: ion-exchange at 80 °C (IE80), ion-exchange at room temperature (IE), and incipient wetness impregnation (IWI).

Table 1. Quantification of H\textsubscript{2} consumption by peak integration of H\textsubscript{2}-TPR profiles of Pd(0.3)-HMOR prepared by different methods.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>$T$ (°C)</th>
<th>H\textsubscript{2}/Pd</th>
<th>μmol H\textsubscript{2}/g\textsubscript{catal}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(0.3)-HMOR(IE80)</td>
<td>85–180</td>
<td>0.8</td>
<td>26</td>
</tr>
<tr>
<td>Pd(0.3)-HMOR(IE)</td>
<td>70–200</td>
<td>0.9</td>
<td>39</td>
</tr>
<tr>
<td>Pd(0.3)-HMOR(IWI)</td>
<td>85–200</td>
<td>1.0</td>
<td>29</td>
</tr>
</tbody>
</table>

In a previous study [11], it was concluded that the reduction peak identified for Pd($x$)-HMOR ($x = 0.15, 0.3, 0.5, \text{ and } 0.7$ wt. %), which are similar to the ones observed for the catalysts presented herein, was actually composed by two different reduction processes (resolved as Gaussian peaks), likely to correspond to Pd\textsuperscript{2+} ions in different exchange positions. The same deconvolution procedure was applied to the H\textsubscript{2}-TPR profiles presented in Figure 1 and the relative distribution of Pd\textsuperscript{2+} ions are presented in Table 2. It should be noted that the Pd(0.3)-HMOR(IWI) possesses a considerably higher amount of Pd\textsuperscript{2+} ions reducible at higher temperature.

Table 2. Quantification of the relative amount of Pd\textsuperscript{2+} corresponding to both reduction process of Pd(0.3)-HMOR prepared by different methods.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Gaussian Peak A</th>
<th>Gaussian Peak B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T$ (°C)</td>
<td>Amount of Pd\textsuperscript{2+}</td>
</tr>
<tr>
<td>Pd(0.3)-HMOR(IE80)</td>
<td>129</td>
<td>78%</td>
</tr>
<tr>
<td>Pd(0.3)-HMOR(IE)</td>
<td>118</td>
<td>69%</td>
</tr>
<tr>
<td>Pd(0.3)-HMOR(IWI)</td>
<td>137</td>
<td>58%</td>
</tr>
</tbody>
</table>
2.1.2. Diffuse Reflectance UV-Vis Spectroscopy (DRS UV-Vis)

Figure 2 illustrates the DRS UV-Vis spectra of Pd-HMOR catalysts containing 0.3 wt. % of Pd, introduced by the three different methods previously mentioned. All spectra exhibit bands around 300–450 nm. In this region, bands are attributed to d-d transitions of Pd$^{2+}$ ions affected by different oxygen environments and/or presence of water (PdO, Pd(H$_2$O)$_4^{2+}$, Pd(O$_2$)$_n^{2+}$) [17]. For instance, a band around 390–410 nm has been assigned to Pd(H$_2$O)$_n^{2+}$ complex [18].

![Figure 2. Diffuse Reflectance UV-Vis spectra of Pd(0.3)-HMOR catalysts prepared by different methods.](image)

Both catalysts prepared by ion-exchange exhibit very similar spectra. However, the spectrum from Pd(0.3)-HMOR(IWI) presents a more pronounced band around 315 nm. Though both bands identified in DRS UV-Vis spectra may correspond to Pd$^{2+}$ ions affected by different oxygen environments, one cannot exclude that each band may, indeed, correspond to Pd$^{2+}$ ions in different locations, as H$_2$-TPR results seem to evidence. It is known that MOR zeolite possesses many different exchange positions where cations can be stabilized in order to compensate the negative charge of framework aluminum [19]. In fact, in a study based on DRS UV-Vis spectroscopy, Kaucký et al. [20] were able to identify three different exchange sites where Co$^{2+}$ ions would be stabilized in MOR. Depending on the site occupied, Co$^{2+}$ would have different activity for NO$_x$ CH$_4$-SCR. Nevertheless, in this work, it was not possible to determine with precision the two possible locations for stabilization of Pd$^{2+}$ ions.

2.1.3. NO$_x$ CH$_4$-SCR

The catalytic performance for NO$_x$ CH$_4$-SCR reaction over Pd(0.3)-HMOR catalysts, prepared by different methods, was assessed (Figure 3). N$_2$O and CO formation are negligible (except at 500 °C, where CH$_4$ conversion into CO is ca. 10% for all catalysts). It should be highlighted that the tests herein presented were conducted in the absence of water in the inlet gas feed. Water is naturally present in the exhaust gases as a product of fuel combustion and usually causes a decrease in catalytic activity, due to the competitive adsorption with the reactants for the active sites. Though the catalytic test in the absence of water cannot be considered representative of real exhaust gas conditions, by performing tests in these
conditions it is possible to obtain higher NO\textsubscript{x} and CH\textsubscript{4} conversions. This will likely facilitate the fundamental study of the effect of preparation methods in the catalytic performance, which is the main goal of this work.

Figure 3. NO\textsubscript{x} conversion into N\textsubscript{2} (A); CH\textsubscript{4} conversion into CO\textsubscript{x} (B) and CH\textsubscript{4} selectivity to SCR (C) over Pd(0.3)-HMOR catalysts prepared by different methods: Pd(0.3)-HMOR(IE80) (♦); Pd(0.3)-HMOR(IE) (■); and Pd(0.3)-HMOR(IWI) (▲). Conditions: 1000 ppm NO, 1000 ppm CH\textsubscript{4}, 7 vol % O\textsubscript{2}, and GHSV of 40000 h\textsuperscript{-1}.

The three catalyst exhibit very similar NO\textsubscript{x} conversion values, though Pd(0.3)-HMOR(IE) exhibits slightly higher ones. Moreover, Pd(0.3)-HMOR(IWI) exhibits slightly higher CH\textsubscript{4} conversion values, when compared to the remaining catalysts. It should also be highlighted that Pd(0.3)-HMOR(IWI) exhibits a CH\textsubscript{4} selectivity towards SCR considerably lower than both catalysts prepared by ion-exchange. This result might be explained due to the stabilization of Pd\textsuperscript{2+} ions species in a specific position that might contribute to the CH\textsubscript{4} direct conversion (combustion) instead of NO\textsubscript{x} SCR, which is in agreement with the evidences obtained by H\textsubscript{2}-TPR and DRS UV-Vis.

Previous works have shown the importance of the preparation methods in the catalytic performance of Pd-based catalysts for NO\textsubscript{x} SCR. For instance, Marques et al. [21] concluded that the use of Pd(NH\textsubscript{3})\textsubscript{4}(NO\textsubscript{3})\textsubscript{2} precursor in the preparation of a Al\textsubscript{2}O\textsubscript{3}-supported palladium catalysts leads to catalysts more active for NO\textsubscript{x} CH\textsubscript{4}-SCR, when compared to the use of other Pd precursors. In the present work,
it is shown that the method chosen for the introduction of Pd is also an important parameter to take into consideration when preparing active catalysts for NOx SCR, namely zeolite-based catalysts.

2.2. The Effect of Pd Loading on Pd/Ce Bimetallic Catalysts

2.2.1. Temperature Programmed Reaction under Hydrogen (H2-TPR)

H2-TPR profiles of Pd(x)Ce(2)-HMOR catalysts \((x = 0, 0.15, 0.3, 0.5\) and 0.7 wt. % Pd) are presented in Figure 4 and the respective quantification of H2 consumption is exhibit in Table 3.

![Figure 4. H2-TPR profiles of Pd(x)Ce(2)-HMOR catalysts.](image)

**Table 3.** Quantification of H2 consumption by peak integration of H2-TPR profiles of Pd(x)Ce(2)-HMOR.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Peak 1</th>
<th>Peak 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(T) (°C)</td>
<td>(H_2/Pd)</td>
</tr>
<tr>
<td>Ce(2)-HMOR</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pd(0.15)Ce(2)-HMOR</td>
<td>80–220</td>
<td>2.9</td>
</tr>
<tr>
<td>Pd(0.3)Ce(2)-HMOR</td>
<td>95–215</td>
<td>1.4</td>
</tr>
<tr>
<td>Pd(0.5)Ce(2)-HMOR</td>
<td>80–220</td>
<td>1.6</td>
</tr>
<tr>
<td>Pd(0.7)Ce(2)-HMOR</td>
<td>75–220</td>
<td>1.4</td>
</tr>
</tbody>
</table>

A similar reduction peak to the ones observed in H2-TPR profiles of monometallic Pd catalysts previously presented is also observed in H2-TPR profiles of the bimetallic catalysts. However, the quantification of the H2 consumption in this region (Table 3) reveals a H2/Pd ratio higher than the unity for all catalysts. As it was described in a previous study considering Pd(0.3)Ce(\(x\))-HMOR catalysts \((x = 1–10\) wt. % Ce) [11], this is related to the presence of surface Ce\(^{4+}\) (CeO\(_2\)) species, whose reduction is known to occur in the same range of temperatures [22]. The highest for Pd(0.15)Ce(2)-HMOR, which means that a considerable amount of H2 consumption is due to the presence of surface CeO\(_2\) species. For 0.3 wt. % Pd, the ratio decreases significantly but the H2 consumption is practically the same. Hence, this catalyst presents less surface CeO\(_2\) species than the previous one. With 0.5 wt. % Pd, the H2/Pd ratio

increases suggesting the stabilization of more surface CeO$_2$ species but with 0.7 wt. % Pd, the ratio decreases again. It is not possible, then, to obtain a correlation between the increasing of surface CeO$_2$ species with the increasing of Pd loading, which suggests that the formation of this species seems to be independent of Pd loading.

In a previous work [11], a second reduction peak in H$_2$-TPR profile of Pd(0.3)Ce(x)-HMOR catalysts, between 240 and 560 °C, has been ascribed to the reduction of CeO$_2$ species in interaction with palladium species. Bulk CeO$_2$ species are usually reduced at higher temperatures. For instance, in Ce(2)-HMOR it is possible to see that the reduction processes only starts at 335 °C and it is extended until 810 °C. For the Pd(x)Ce(2)-HMOR catalysts considered in this study, H$_2$/Ce ratio resulting from the quantification of the previous mentioned peak also seems to be independent of Pd loading (it increases from 0.15 to 0.3 wt. % Pd, then decreases from 0.3 to 0.5 wt. % Pd and increases again from 0.5 to 0.7 wt. % Pd). Notwithstanding, it is interesting to notice that the stabilization of CeO$_2$ species in interaction Pd species follows an opposite trend to the one verified for surface CeO$_2$ species, i.e., when the H$_2$/Ce ratio of CeO$_2$ interacting species increase, the H$_2$/Pd ratio decreases, and *vice versa*.

2.2.2. Diffuse Reflectance UV-Vis Spectroscopy (DRS UV-Vis)

Figure 5 exhibits the DRS UV-Vis spectra of Pd(x)Ce(2)-HMOR catalysts considered in this work.

![Figure 5. Diffuse Reflectance UV-Vis spectra of Pd(x)Ce(2)-HMOR catalysts.](image_url)

As previously identified for the monometallic Pd catalysts, the bands near 380 nm are characteristic of Pd$^{2+}$ species. The fact that it appears slightly blue-shifted, may be due to the presence of Ce [11]. The bands at 260 and 290 are ascribed to transition 4f-5d of Ce$^{3+}$ and to charge transfer from O$^{2-}$ to Ce$^{4+}$ in CeO$_2$ clusters, respectively [23,24]. The band at 240 nm is ascribed to the charge transfer Pd→O [25].

From the spectra analysis, it is possible to observe that the band at 240 nm becomes more pronounced with the increasing of Pd loading, which was expected. A similar increase in the band around 380 nm would be also expected, though not observed. The reason might be the interference of the cerium characteristics bands.
2.2.3. NO\textsubscript{x} CH\textsubscript{4}-SCR

Steady-state catalytic test results obtained for Pd(x)Ce(2)-HMOR catalysts are exhibit in Figure 6. CO formation is negligible and not presented.

For temperatures below 450 °C, NO\textsubscript{x} conversion values are very similar for Pd loadings of 0.3–0.7 wt. %. Only for 0.15 wt. % Pd, NO\textsubscript{x} conversion is significantly lower in practically the entire range of temperatures. In a previous work conducted by the authors [11], it has been reported that Pd(0.15)-HMOR also presented lower conversion values, when compared to Pd(x)-HMOR catalysts, with 0.3–0.7 wt. % Pd. This behavior was attributed to the low content of Pd, namely Pd\textsuperscript{2+} ions, which are known to be active species for the NO\textsubscript{x} CH\textsubscript{4}-SCR [26] and this is likely to be the explanation for the lower activity of Pd(0.15)Ce(2)-HMOR, when compared to the other catalysts.
Similarly to what was reported for the monometallic Pd(x)-HMOR catalysts [11], the increase of the Pd loading in bimetallic PdCe-HMOR catalysts decreases the NOx conversion into N2 and promotes N2O formation instead. It should be highlighted that in the previous mentioned study, Pd(0.3)Ce(x)-HMOR catalysts (x = 1–10 wt. %) were tested in the same conditions and N2O formation was practically negligible, which excludes the effect of cerium in the N2O formation. These findings suggest, then, that Pd species are the ones directly related to the selectivity of NOx towards N2 and that cerium species do not determine this parameter.

As well as for monometallic Pd-MOR catalysts, CH4 direct combustion over Pd(x)Ce(2)-HMOR catalysts increases with the increase of Pd loading. Palladium-loaded catalysts are also used as hydrocarbon oxidation catalysts [27,28]. Hence, it is also likely that Pd species, together with CeO2 species, known for having oxidative properties, play a role in the CH4 direct combustion.

Based on the catalytic test results obtained, one can say that Pd(0.3)Ce(2)-HMOR is the catalyst that presents the better performance for NOx CH4-SCR in the conditions considered in this work, since it is the one that allows to obtain higher NOx conversion into N2 values using CH4 more efficiently, as a reductant (i.e., higher CH4 selectivity towards SCR).

2.3. The Effect of Metal Introduction Order

2.3.1. Temperature Programmed Reaction under Hydrogen (H2-TPR)

Figure 7 illustrates the H2-TPR profiles of PdCe-HMOR catalysts, containing 0.3 wt. % Pd and 2 wt. % Ce, where metals were introduced in different order. The quantification of H2 consumption can be found in Table 4.

The results show that (Table 4), on one hand, when cerium is introduced before palladium (Ce(2)Pd(0.3)-HMOR), the H2 consumption corresponding to the low-temperature reduction processes (<220 °C) increases, which means that the amount of surface CeO2 species increases.

On the other hand, H2 consumption in the region 240–560 °C decreases, meaning that the amount of CeO2 species interacting with palladium also decreases.

![Figure 7.](image)
Table 4. Quantification of H₂ consumption by peak integration of H₂-TPR profiles of Pd(0.3)Ce(2)-HMOR with metals introduced in different order.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Peak 1</th>
<th>Peak 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T (°C)</td>
<td>H₂/Pd</td>
</tr>
<tr>
<td>Pd(0.3)Ce(2)-HMOR</td>
<td>95–215</td>
<td>1.4</td>
</tr>
<tr>
<td>Ce(2)Pd(0.3)-HMOR</td>
<td>70–220</td>
<td>1.9</td>
</tr>
</tbody>
</table>

2.3.2. Diffuse Reflectance UV-Vis Spectroscopy (DRS UV-Vis)

Figure 8 exhibits the DRS UV-Vis spectra of PdCe-HMOR catalysts, containing 0.3 wt. % Pd and 2 wt. % Ce, where metals were introduced in different orders.

![Figure 8. Diffuse Reflectance UV-Vis spectra of PdCe-HMOR catalysts containing 0.3 wt. % Pd and 2 wt. % Ce, introduced in different order.](image)

Both spectra exhibit three similar bands at 260, 290, and 380 nm attributed to Ce³⁺, Ce⁴⁺, and Pd²⁺ species, respectively. However, a forth band at 470 nm is observed in the Ce(2)Pd(0.3)-HMOR spectrum. As it was already mentioned, bands in this zone are characteristic of d-d transition of Pd²⁺ ions affected by different oxygen environments. Again, in this case, one cannot exclude the existence of two different Pd²⁺ species, which might be a result of the presence of Ce, when Pd was introduced.

2.3.3. NOₓ CH₄-SCR

Figure 9 compares the steady-state catalytic test results of both PdCe-HMOR catalysts, containing 0.3 wt. % Pd and 2 wt. % Ce, where metals were introduced in different order. N₂O and CO conversions are negligible and not shown.

In the entire range of temperature, Ce(2)Pd(0.3)-HMOR (Ce introduced first) presents higher CH₄ conversion values than Pd(0.3)Ce(2)-HMOR. For temperatures below 450 °C, NOₓ conversions are practically the same. In fact, it is possible to observe that CH₄ selectivity towards SCR of Ce(2)Pd(0.3)-HMOR is significantly lower than Pd(0.3)Ce(2)-HMOR. At 500 °C, NOₓ conversion for Ce(2)Pd(0.3)-HMOR decreases and becomes significantly lower than Pd(0.3)Ce(2)-HMOR, which can be explained due to the lack of reductant available for the reaction.
Figure 9. NO\textsubscript{x} conversion into N\textsubscript{2} (A); CH\textsubscript{4} conversion into CO\textsubscript{2} (B) and CH\textsubscript{4} selectivity to SCR reaction (C) over PdCe-HMOR catalysts containing 0.3 wt. % Pd and 2 wt. % Ce, introduced in different order. Conditions: 1000 ppm NO; 1000 ppm CH\textsubscript{4}, 7 vol % O\textsubscript{2}; and GHSV of 40000 h\textsuperscript{-1}.

Characterization of Ce(2)Pd(0.3)-HMOR evidenced a possible existence of different Pd species, compared to Pd(0.3)Ce(2)-HMOR. Though the analysis of H\textsubscript{2}-TPR profile in the low-temperature region does not allow one to obtain a distribution of Pd\textsuperscript{2+} species as it was previously presented for the monometallic catalysts (due to the presence of surface CeO\textsubscript{2} species), one cannot exclude a change in the Pd species distributions when Ce has been already introduced. Likewise, the contribution of surface CeO\textsubscript{2} species for CH\textsubscript{4} direct oxidation cannot be excluded. Finally, it should be noted that CeO\textsubscript{2} species in interaction with Pd species seem to be less when Ce is introduced first. In a previous work [11], it has been suggested the importance of this species for the NO\textsubscript{x} CH\textsubscript{4}-SCR. Hence, it is likely that their decrease can also contribute to a worse catalytic performance of Ce(2)Pd(0.3)-HMOR.

3. Experimental Section

3.1. Catalyst Preparation

Catalysts were prepared from CBV21A zeolite (NH\textsubscript{4}MOR), with Si/Al = 10 supplied by Zeolyst International. Monometallic Pd-zeolites were obtained by three different methods. Pd(0.3)-HMOR(IE)
was prepared by ion exchanging the NH₄MOR zeolite with a solution with adequate concentration, prepared by dilution of a Pd(NH₃)₄(NO₃)₂ aqueous solution (99.99% purity, 10 wt. %, supplied by Aldrich, Lisbon, Portugal), for 24 h, at room temperature. Afterwards, exchanged samples were recovered by centrifugation and dried in an oven at 90 °C, overnight. Pd-zeolites were then calcined under air flow, at 500 °C, for 1 h (1 °C/min). Pd(0.3)-HMOR(IE80) was prepared based on the procedure described elsewhere [29], consisting in ion exchanging the NH₄MOR zeolite with a solution with adequate concentration, prepared by dilution of a Pd(NH₃)₄(NO₃)₂ aqueous solution, for 24 h, at 80 °C. The same drying and calcination procedures previously described were applied (except the heating rate considered for the calcination: 0.5 °C/min). Pd(0.3)-HMOR(IWI) was obtained by introducing Pd by the incipient wetness impregnation technique, using a Pd(NH₃)₄(NO₃)₂ solution with adequate concentration. Drying and calcination procedures were performed as for Pd(0.3)-HMOR(IE).

Bimetallic Pd(\(x\))Ce(2)-HMOR were obtained from Pd(\(x\))-HMOR (\(x = 0.15, 0.3, 0.5\) and 0.7 wt. %), previously prepared as Pd(0.3)-HMOR(IE), by introducing cerium by the incipient wetness impregnation technique, using a solution with adequate concentration, prepared with Ce(NO₃)₃·6H₂O salt (99% purity, supplied by Fluka, Lisbon, Portugal). Then, samples were dried in an oven at 90 °C, overnight, and finally calcined at 500 °C, for 8 h (5 °C/min).

Finally, Ce(2)Pd(0.3)-HMOR catalyst was obtained from Ce(2)-HMOR, previously prepared by introducing Ce by IWI, as described for Pd(\(x\))Ce(2)-HMOR catalysts, but using NH₄MOR as starting material. Then, Pd was introduced by ion exchange, following the same procedure previously described for Pd(0.3)-HMOR(IE).

Table 5 illustrates the chemical composition of all catalysts considered in this study, obtained by ICP analysis.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Al (wt. %)</th>
<th>Pd (wt. %)</th>
<th>Ce (wt. %)</th>
<th>ERₚd * (%)</th>
<th>ERₙCe * (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(0.3)-HMOR(IE80)</td>
<td>3.6</td>
<td>0.35</td>
<td>-</td>
<td>5.0</td>
<td>-</td>
</tr>
<tr>
<td>Pd(0.3)-HMOR(IE)</td>
<td>3.3</td>
<td>0.36</td>
<td>-</td>
<td>5.5</td>
<td>-</td>
</tr>
<tr>
<td>Pd(0.3)-HMOR(IWI)</td>
<td>3.1</td>
<td>0.30</td>
<td>-</td>
<td>4.8</td>
<td>-</td>
</tr>
<tr>
<td>Ce(2)-HMOR</td>
<td>3.3</td>
<td>-</td>
<td>2.1</td>
<td>-</td>
<td>36.6</td>
</tr>
<tr>
<td>Pd(0.15)Ce(2)-HMOR</td>
<td>3.2</td>
<td>0.15</td>
<td>1.8</td>
<td>2.4</td>
<td>32.9</td>
</tr>
<tr>
<td>Pd(0.3)Ce(2)-HMOR</td>
<td>3.4</td>
<td>0.29</td>
<td>1.9</td>
<td>4.3</td>
<td>32.2</td>
</tr>
<tr>
<td>Pd(0.5)Ce(2)-HMOR</td>
<td>3.3</td>
<td>0.52</td>
<td>1.7</td>
<td>7.9</td>
<td>29.6</td>
</tr>
<tr>
<td>Pd(0.7)Ce(2)-HMOR</td>
<td>3.2</td>
<td>0.70</td>
<td>1.9</td>
<td>11.3</td>
<td>35.0</td>
</tr>
<tr>
<td>Ce(2)Pd(0.3)-HMOR</td>
<td>3.2</td>
<td>0.42</td>
<td>1.8</td>
<td>6.8</td>
<td>33.6</td>
</tr>
</tbody>
</table>

* ER—Exchange Rate (Assuming 2+ and 3+ coordination for Pd and Ce, respectively).

3.2. Catalyst Characterization

Temperature programmed reduction under hydrogen (H₂-TPR) was performed by contacting a catalyst sample (ca. 100 mg) with a mixture of H₂ (5 vol %)/Ar and heating it until 900 °C using a ramp of 7.5 °C/min. Hydrogen consumption was measured with a thermal conductivity detector. Water was removed in a dry ice-cooled trap.
Diffuse reflectance UV-Vis spectroscopy (DRS UV-Vis) were performed using a Varian Cary 5000 UV-Vis-NIR spectrophotometer (at CQE, Lisbon, Portugal) equipped with a Praying Mantis accessory (from Harrick). Spectra were collected at room temperature, using calcined samples (range 200–800 nm, scan rate—600 nm/min, data interval—1 nm, SBW—4 nm). Reflectance spectra were converted into the Schuster-Kubelka-Munk (SKM) function, F(R), calculated at each wavelength using the Equation (1):

$$F(R) = \frac{(1 - R)^2}{2R}$$

(1)

$R$ is the ratio of the intensity of the light reflected by the sample to the one reflected by a standard. In order to minimize the effect of zeolite framework absorption, the standard considered was a parent HMOR zeolite sample, obtained from NH4MOR, by following the same calcination procedure described for Ce-containing catalysts, after Ce introduction.

### 3.3. Catalyst Tests

Steady-state catalytic tests were performed in a tubular pyrex reactor (homemade, at IST, Lisbon, Portugal) using 190 mg of catalyst (dry basis). Before the reaction, a pre-treatment was performed in order to clean the catalysts’ surface, consisting in heating the catalyst under argon flow (15 L/h), from room temperature to 500 °C (5 °C/min) and keeping this temperature for 1 h. Then, the reactor was cooled to 300 °C. Meanwhile, the reaction mixture was stabilized in a reactor bypass, using two four-way valves. Once stable, the reaction mixture was fed to the reactor. When the steady-state was reached, the temperature was raised 50 °C and the procedure was repeated until 500 °C.

NO\textsubscript{x} SCR tests were performed using a mixture of 1000 ppm NO, 1000 ppm CH\textsubscript{4} and 7 vol % O\textsubscript{2} in flowing argon (total flow rate of 15 L/h, GHSV = 40000 h\textsuperscript{-1}).

The reactor’s outflow was continuously analyzed. NO and NO\textsubscript{2} concentrations were detected by a Thermo 42C chemiluminescence analyzer and CO, CO\textsubscript{2} and N\textsubscript{2}O concentrations were detected by an ABB EL 3020 infrared analyzer.

For each temperature $T$, NO\textsubscript{x} conversion into N\textsubscript{2} and N\textsubscript{2}O was obtained using Equations (2) and (3), respectively. CH\textsubscript{4} conversion into CO\textsubscript{x} was obtained using Equation (4) and selectivity of CH\textsubscript{4} towards SCR reaction was obtained using Equation (5).

$$x_{NO_x \rightarrow N_2,T}(\%) = \left(1 - \frac{n_{NO,T} + n_{NO_2,T} + 2n_{N_2O,T}}{n_{NO,0} + n_{NO_2,0}}\right) \times 100\%$$

(2)

$$x_{NO_x \rightarrow N_2O,T}(\%) = \frac{2n_{N_2O,T}}{n_{NO,0} + n_{NO_2,0}} \times 100\%$$

(3)

$$x_{CH_4 \rightarrow CO_x,T}(\%) = \frac{n_{CO_2,T} + n_{CO,T}}{n_{CH_4,0}} \times 100\%$$

(4)

$$S_{\text{CH}_4 \text{to SCR},T}(\%) = \frac{n_{\text{CH}_4 \text{ for SCR},T}}{n_{\text{CH}_4 \text{ converted},T}} = \frac{1}{2} \frac{n_{NO,0} + n_{NO_2,0} - (n_{NO,T} + n_{NO_2,T} + 2n_{N_2O,T})}{n_{CH_4,0} - (n_{CO_2,T} + n_{CO,T})} \times 100\%$$

(5)
0 represents the initial condition (by-pass mixture) before starting the reaction. \( n_i \) is the molar flow of component \( i \).

4. Conclusions

In this work, the effect of several parameters related to the preparation of active PdCe-HMOR to be used as NO\(_x\)-CH\(_4\)-SCR system, suitable for natural gas vehicle applications, were studied.

It was shown that the palladium introduction method influences the catalytic performance of Pd/zeolite-based catalysts. When Pd is introduced by ion exchange, a better catalytic performance is achieved.

The influence of Pd loading in bimetallic PdCe-HMOR system was also assessed. It was shown that Pd loading does not influence the stabilization of Ce species. However, it was observed that, when Pd is introduced before Ce, a better catalytic performance can be achieved. When Ce is introduced first, more surface CeO\(_2\) species are stabilized and less CeO\(_2\) species in interaction with Pd are present in the catalyst, which results in a lower CH\(_4\) selectivity towards SCR.

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Author Contributions

A.N.M., C.H. and P.D.C. conceived and designed the experiments. A.N.M. performed the experiments. A.N.M., M.F.R., C.H., and P.D.C. analyzed the data. A.N.M. wrote the paper and M.F.R., C.H. and P.D.C. revised it.

Conflicts of Interest

The authors declare no conflict of interest.

References


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