



HAL
open science

On the Effect of Preparation Methods of PdCe-MOR Catalysts as NO_x CH₄-SCR System for Natural Gas Vehicles Application

Acácio Mendes, Maria Ribeiro, Carlos Henriques, Patrick da Costa

► **To cite this version:**

Acácio Mendes, Maria Ribeiro, Carlos Henriques, Patrick da Costa. On the Effect of Preparation Methods of PdCe-MOR Catalysts as NO_x CH₄-SCR System for Natural Gas Vehicles Application. Catalysts, 2015, 5 (4), pp.1815-1830. 10.3390/catal5041815 . hal-01260508

HAL Id: hal-01260508

<https://hal.sorbonne-universite.fr/hal-01260508>

Submitted on 22 Jan 2016

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License

Article

On the Effect of Preparation Methods of PdCe-MOR Catalysts as NO_x CH₄-SCR System for Natural Gas Vehicles Application

Acácio Nobre Mendes ^{1,2}, Maria Filipa Ribeiro ¹, Carlos Henriques ¹ and Patrick Da Costa ^{2,3,*}

¹ Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, Lisboa 1049-001, Portugal; E-Mails: acacio.mendes@tecnico.ulisboa.pt (A.N.M.); filipa.ribeiro@tecnico.ulisboa.pt (M.F.R.); carlos.henriques@tecnico.ulisboa.pt (C.H.)

² Sorbonne Universités, UPMC Université Paris 06, UMR 7190, Institut Jean le Rond d'Alembert, Paris F-75005, France

³ Institut Jean le Rond d'Alembert, UMR 7190, CNRS, Saint-Cyr-l'École F-78210, France

* Author to whom correspondence should be addressed; E-Mail: patrick.da_costa@upmc.fr; Tel.: +33-1-30-85-48-62; Fax: +33-1-30-85-48-99.

Academic Editor: Jae-Soon Choi

Received: 1 September 2015 / Accepted: 12 October 2015 / Published: 27 October 2015

Abstract: In the present work, the effect of several parameters involved in the preparation of PdCe-HMOR catalysts active for NO_x selective catalytic reduction with methane (NO_x CH₄-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 Ce⁴⁺ (CeO₂) species and CeO₂ species in interaction with Pd. However, when Ce is introduced before Pd, more surface CeO₂ species are stabilized in the support and less CeO₂ become in interaction with Pd, which results in a worse NO_x CH₄-SCR catalytic performance.

Keywords: NO_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 [1], 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 the 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 Pd²⁺ ions in exchange positions.

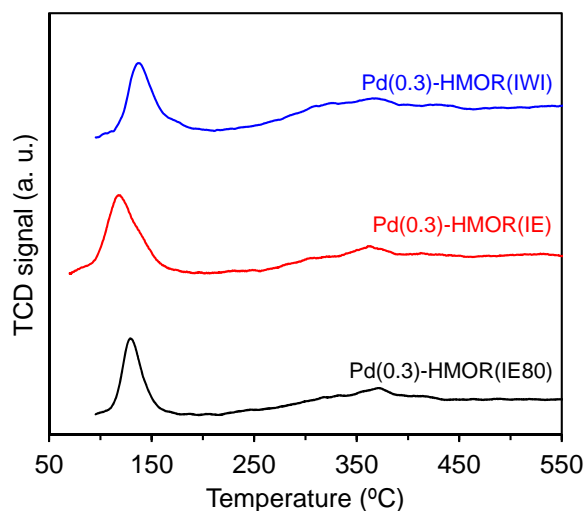


Figure 1. H₂-TPR profiles of Pd(0.3)-HMOR catalysts prepared by different methods: ion-exchange at 80 °C (IE80), ion-exchange at room temperature (IE), and incipient wetness impregnation (IWI).

Table 1. Quantification of H₂ consumption by peak integration of H₂-TPR profiles of Pd(0.3)-HMOR prepared by different methods.

Catalysts	T (°C)	H ₂ /Pd	μmol H ₂ /g _{catal}
Pd(0.3)-HMOR(IE80)	85–180	0.8	26
Pd(0.3)-HMOR(IE)	70–200	0.9	39
Pd(0.3)-HMOR(IWI)	85–200	1.0	29

In a previous study [11], it was concluded that the reduction peak identified for Pd(*x*)-HMOR (*x* = 0.15, 0.3, 0.5, 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 Pd²⁺ ions in different exchange positions. The same deconvolution procedure was applied to the H₂-TPR profiles presented in Figure 1 and the relative distribution of Pd²⁺ ions are presented in Table 2. It should be noted that the Pd(0.3)-HMOR(IWI) possesses a considerably higher amount of Pd²⁺ ions reducible at higher temperature.

Table 2. Quantification of the relative amount of Pd²⁺ corresponding to both reduction process of Pd(0.3)-HMOR prepared by different methods.

Catalysts	Gaussian Peak A		Gaussian Peak B	
	T (°C)	Amount of Pd ²⁺	T (°C)	Amount of Pd ²⁺
Pd(0.3)-HMOR(IE80)	129	78%	144	22%
Pd(0.3)-HMOR(IE)	118	69%	141	31%
Pd(0.3)-HMOR(IWI)	137	58%	152	42%

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 Pd²⁺ ions affected by different oxygen environments and/or presence of water (PdO, Pd(H₂O)₄²⁺; Pd(O_z)_n²⁺) [17]. For instance, a band around 390–410 nm has been assigned to Pd(H₂O)_n²⁺ complex [18].

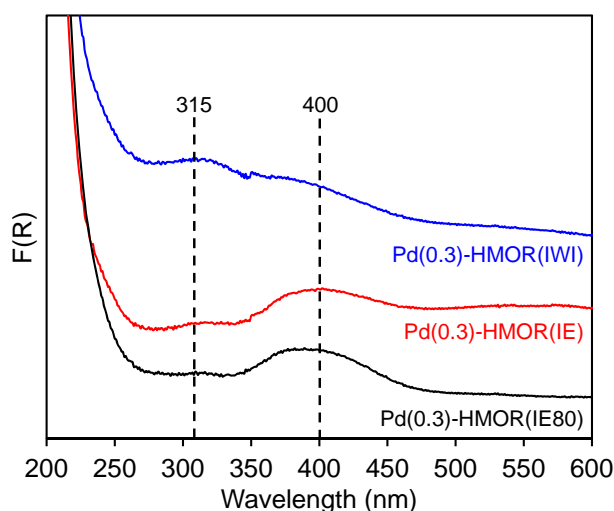


Figure 2. Diffuse Reflectance UV-Vis spectra of Pd(0.3)-HMOR catalysts prepared by different methods.

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 Pd²⁺ ions affected by different oxygen environments, one cannot exclude that each band may, indeed, correspond to Pd²⁺ ions in different locations, as H₂-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 Co²⁺ ions would be stabilized in MOR. Depending on the site occupied, Co²⁺ would have different activity for NO_x CH₄-SCR. Nevertheless, in this work, it was not possible to determine with precision the two possible locations for stabilization of Pd²⁺ ions.

2.1.3. NO_x CH₄-SCR

The catalytic performance for NO_x CH₄-SCR reaction over Pd(0.3)-HMOR catalysts, prepared by different methods, was assessed (Figure 3). N₂O and CO formation are negligible (except at 500 °C, where CH₄ 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_x and CH₄ 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.

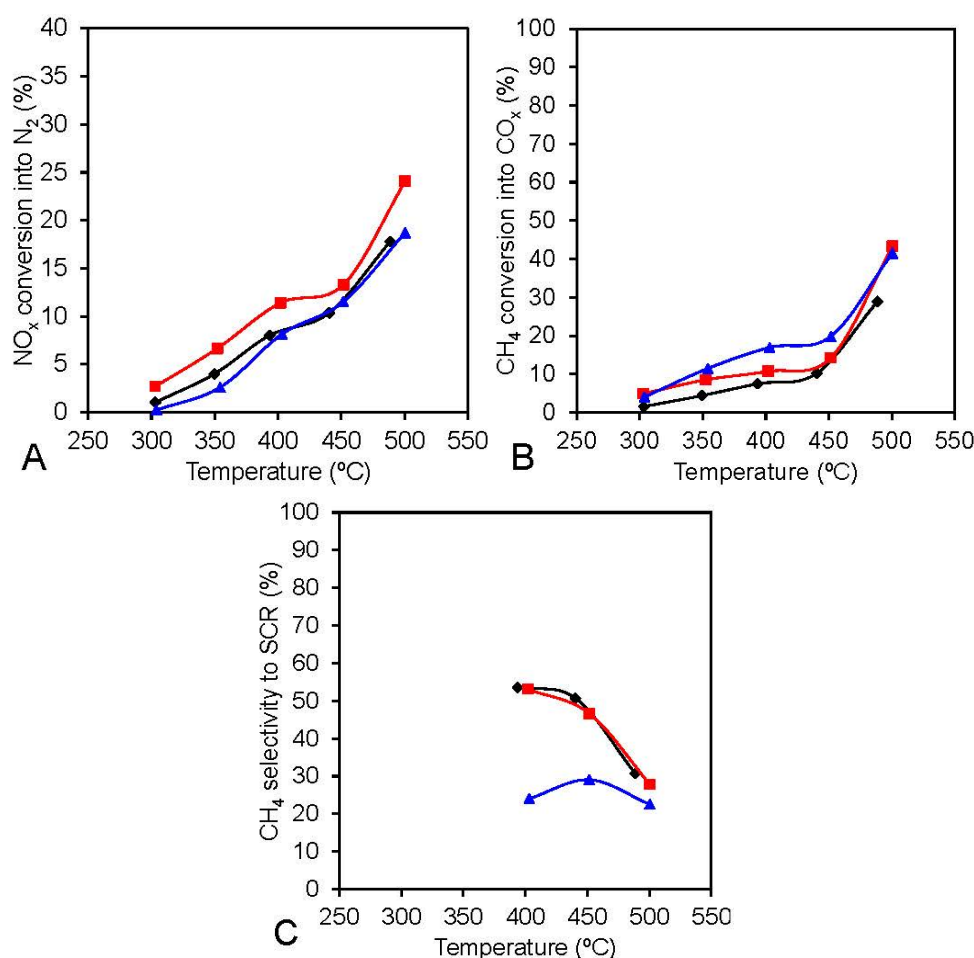


Figure 3. NO_x conversion into N₂ (A); CH₄ conversion into CO_x (B) and CH₄ selectivity to SCR (C) over Pd(0.3)-HMOR catalysts prepared by different methods: Pd(0.3)-HMOR(IE80) (◆); Pd(0.3)-HMOR(IE) (■); and Pd(0.3)-HMOR(IWI) (▲). Conditions: 1000 ppm NO, 1000 ppm CH₄, 7 vol % O₂, and GHSV of 40000 h⁻¹.

The three catalyst exhibit very similar NO_x conversion values, though Pd(0.3)-HMOR(IE) exhibits slightly higher ones. Moreover, Pd(0.3)-HMOR(IWI) exhibits slightly higher CH₄ conversion values, when compared to the remaining catalysts. It should also be highlighted that Pd(0.3)-HMOR(IWI) exhibits a CH₄ selectivity towards SCR considerably lower than both catalysts prepared by ion-exchange. This result might be explained due to the stabilization of Pd²⁺ ions species in a specific position that might contribute to the CH₄ direct conversion (combustion) instead of NO_x SCR, which is in agreement with the evidences obtained by H₂-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_x SCR. For instance, Marques *et al.* [21] concluded that the use of Pd(NH₃)₄(NO₃)₂ precursor in the preparation of a Al₂O₃-supported palladium catalysts leads to catalysts more active for NO_x CH₄-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 NO_x 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.

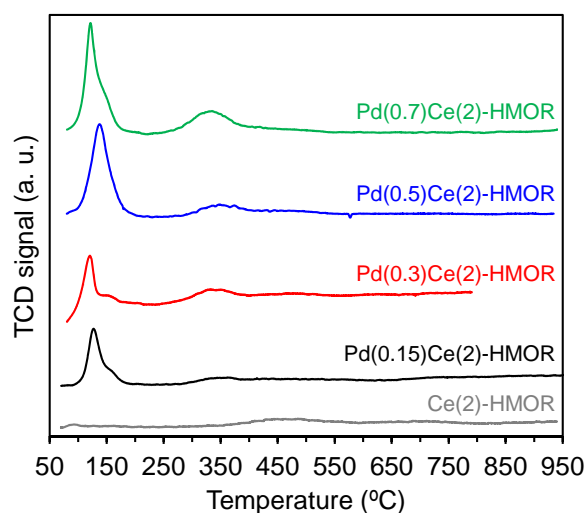


Figure 4. H₂-TPR profiles of Pd(*x*)Ce(2)-HMOR catalysts.

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

Catalysts	Peak 1			Peak 2		
	<i>T</i> (°C)	H ₂ /Pd	μmol H ₂ /g _{catal.}	<i>T</i> (°C)	H ₂ /Ce	μmol H ₂ /g _{catal.}
Ce(2)-HMOR	-	-	-	335–810	0.13	19
Pd(0.15)Ce(2)-HMOR	80–220	2.9	40	265–560	0.11	14
Pd(0.3)Ce(2)-HMOR	95–215	1.4	39	240–560	0.28	37
Pd(0.5)Ce(2)-HMOR	80–220	1.6	80	260–555	0.24	29
Pd(0.7)Ce(2)-HMOR	75–220	1.4	91	240–560	0.38	51

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 Ce⁴⁺ (CeO₂) 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 CeO₂ species. For 0.3 wt. % Pd, the ratio decreases significantly but the H₂ consumption is practically the same. Hence, this catalyst presents less surface CeO₂ 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 $\text{Pd}(0.3)\text{Ce}(x)$ -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 $\text{Ce}(2)$ -HMOR it is possible to see that the reduction processes only starts at 335 °C and it is extended until 810 °C. For the $\text{Pd}(x)\text{Ce}(2)$ -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 $\text{Pd}(x)\text{Ce}(2)$ -HMOR catalysts considered in this work.

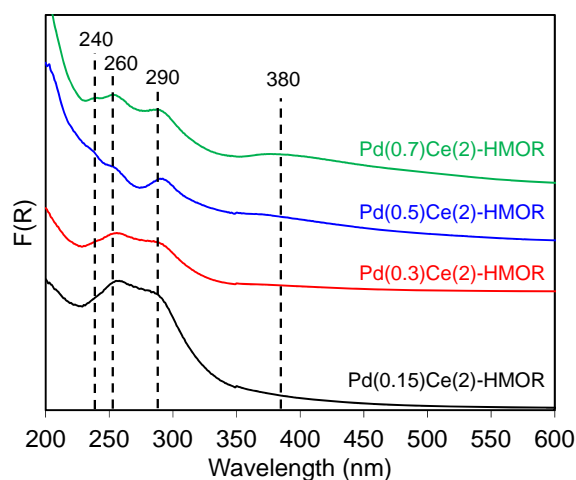


Figure 5. Diffuse Reflectance UV-Vis spectra of $\text{Pd}(x)\text{Ce}(2)$ -HMOR catalysts.

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 $\text{Pd} \rightarrow \text{O}$ [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_x CH₄-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.

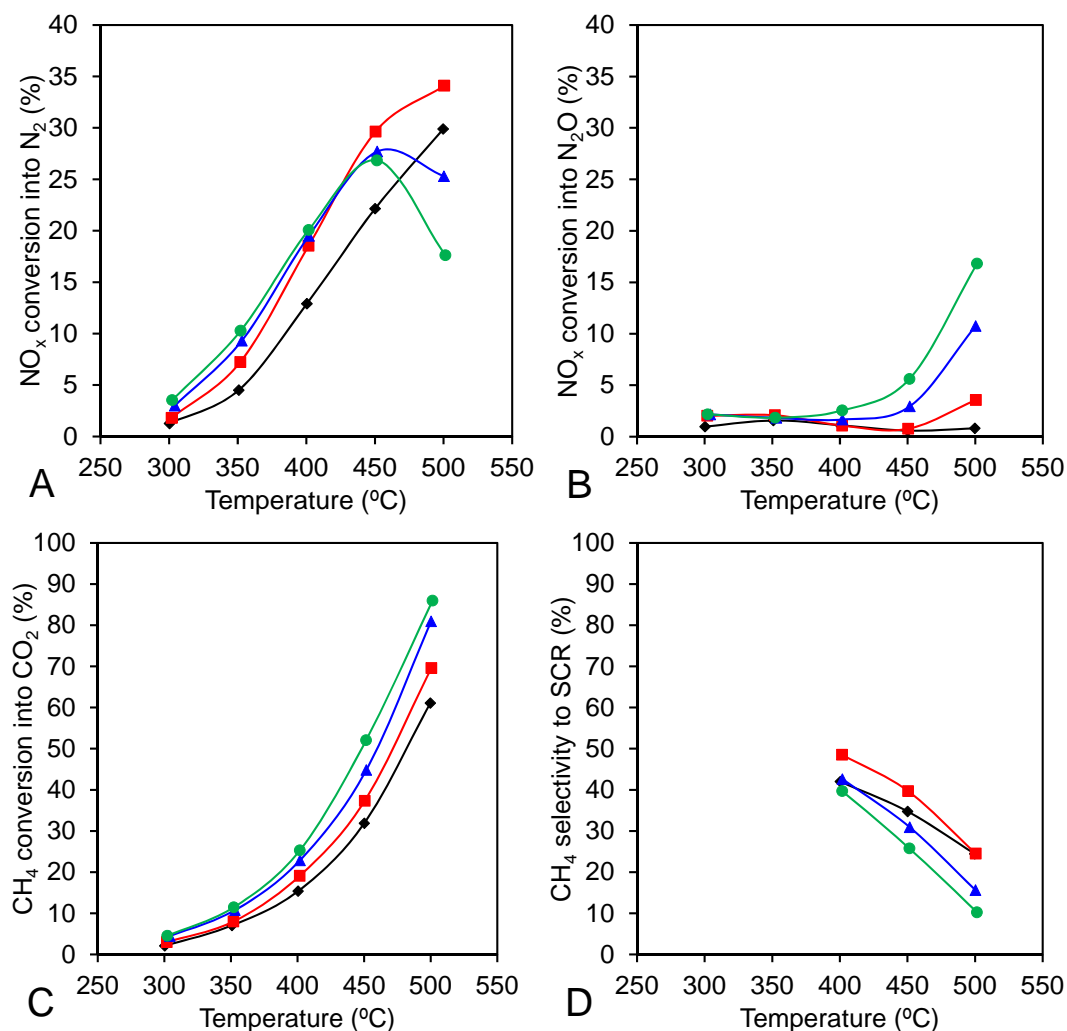


Figure 6. NO_x conversion into N₂ (A) and into N₂O (B); CH₄ conversion into CO₂ (C); and CH₄ selectivity to SCR reaction (D) over PdCe-HMOR containing 2 wt. % of Ce and different loadings of Pd with 1000 ppm NO, 1000 ppm CH₄, 7 vol % O₂, and GHSV of 40,000 h⁻¹: Pd(0.15)Ce(2)-HMOR (◆); Pd(0.3)Ce(2)-HMOR (■), Pd(0.5)Ce(2)-HMOR (▲), and Pd(0.7)Ce(2)-HMOR (●).

For temperatures below 450 °C, NO_x conversion values are very similar for Pd loadings of 0.3–0.7 wt. %. Only for 0.15 wt. % Pd, NO_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 Pd²⁺ ions, which are known to be active species for the NO_x CH₄-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 NO_x 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 NO_x 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 NO_x CH₄-SCR in the conditions considered in this work, since it is the one that allows to obtain higher NO_x 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

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.

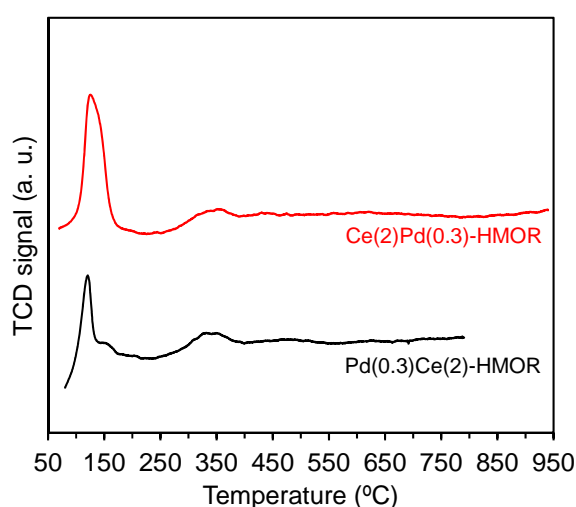


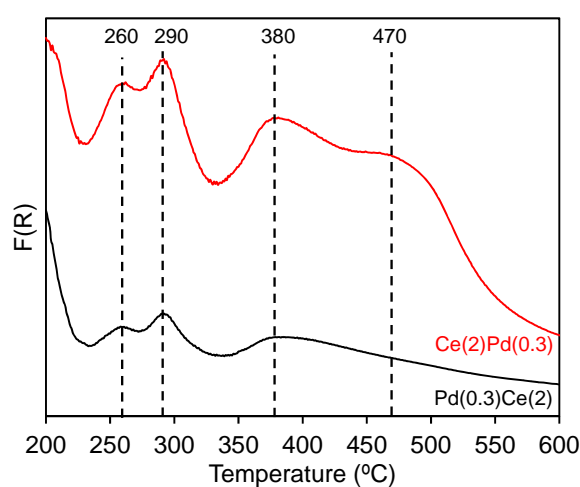
Figure 7. H₂-TPR profiles of PdCe-HMOR catalysts containing 0.3 wt. % Pd and 2 wt. % Ce, introduced in different orders.

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.

Catalysts	Peak 1			Peak 2		
	T (°C)	H ₂ /Pd	μmol H ₂ /g _{catal.}	T (°C)	H ₂ /Ce	μmol H ₂ /g _{catal.}
Pd(0.3)Ce(2)-HMOR	95–215	1.4	39	240–560	0.28	37
Ce(2)Pd(0.3)-HMOR	70–220	1.9	76	250–560	0.25	32

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.

Both spectra exhibit three similar bands at 260, 290, and 380 nm attributed to Ce³⁺, Ce⁴⁺, and Pd²⁺ species, respectively. However, a fourth 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. NO_x 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, NO_x 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, NO_x 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.

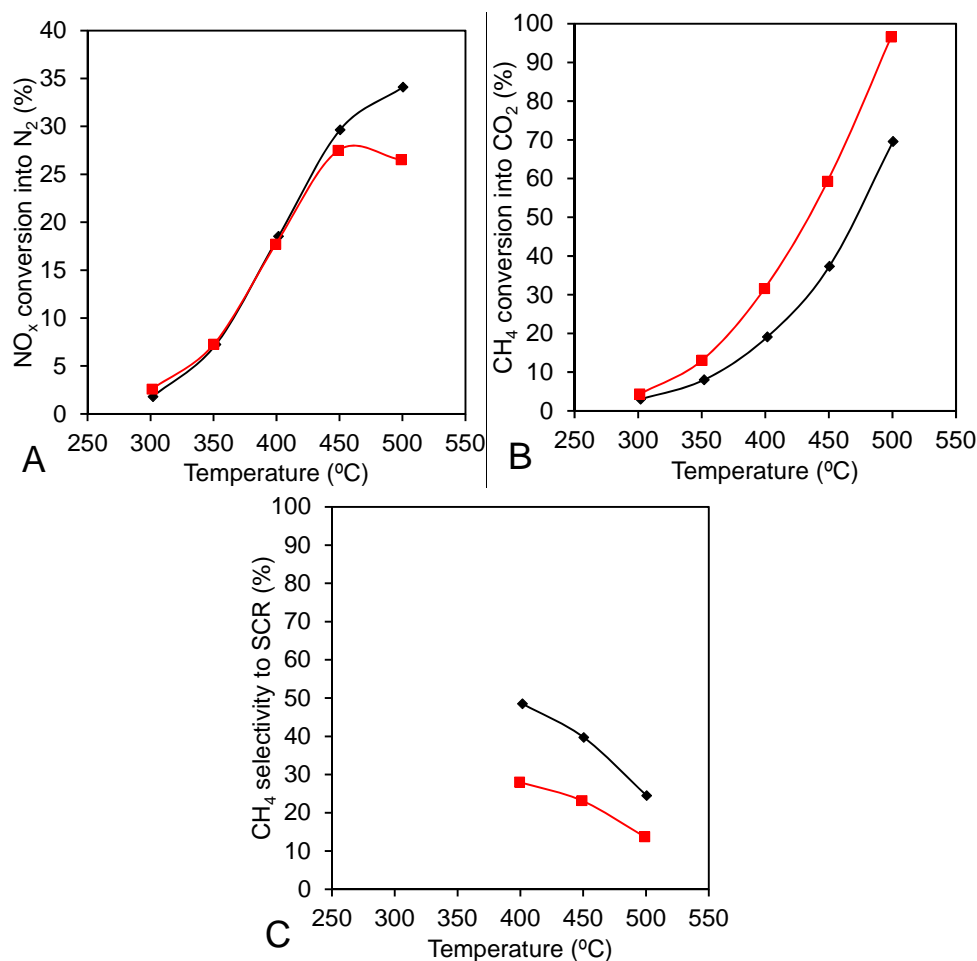


Figure 9. NO_x conversion into N₂ (A); CH₄ conversion into CO₂ (B) and CH₄ selectivity to SCR reaction (C) over PdCe-HMOR catalysts containing 0.3 wt. % Pd and 2 wt. % Ce, introduced in different order. Conditions: 1000 ppm NO; 1000 ppm CH₄, 7 vol % O₂; and GHSV of 40000 h⁻¹.

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 H₂-TPR profile in the low-temperature region does not allow one to obtain a distribution of Pd²⁺ species as it was previously presented for the monometallic catalysts (due to the presence of surface CeO₂ species), one cannot exclude a change in the Pd species distributions when Ce has been already introduced. Likewise, the contribution of surface CeO₂ species for CH₄ direct oxidation cannot be excluded. Finally, it should be noted that CeO₂ 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_x CH₄-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 (NH₄MOR), 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 5. Chemical composition of the catalysts obtained by ICP-OES analysis.

Catalysts	Al (wt. %)	Pd (wt. %)	Ce (wt. %)	ER _{Pd} * (%)	ER _{Ce} * (%)
Pd(0.3)-HMOR(IE80)	3.6	0.35	-	5.0	-
Pd(0.3)-HMOR(IE)	3.3	0.36	-	5.5	-
Pd(0.3)-HMOR(IWI)	3.1	0.30	-	4.8	-
Ce(2)-HMOR	3.3	-	2.1	-	36.6
Pd(0.15)Ce(2)-HMOR	3.2	0.15	1.8	2.4	32.9
Pd(0.3)Ce(2)-HMOR	3.4	0.29	1.9	4.3	32.2
Pd(0.5)Ce(2)-HMOR	3.3	0.52	1.7	7.9	29.6
Pd(0.7)Ce(2)-HMOR	3.2	0.70	1.9	11.3	35.0
Ce(2)Pd(0.3)-HMOR	3.2	0.42	1.8	6.8	33.6

* 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):

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

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 NH_4MOR , 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_x SCR tests were performed using a mixture of 1000 ppm NO, 1000 ppm CH_4 and 7 vol % O_2 in flowing argon (total flow rate of 15 L/h, GHSV = 40000 h^{-1}).

The reactor's outflow was continuously analyzed. NO and NO_2 concentrations were detected by a Thermo 42C chemiluminescence analyzer and CO, CO_2 and N_2O concentrations were detected by an ABB EL 3020 infrared analyzer.

For each temperature T , NO_x conversion into N_2 and N_2O was obtained using Equations (2) and (3), respectively. CH_4 conversion into CO_x was obtained using Equation (4) and selectivity of CH_4 towards SCR reaction was obtained using Equation (5).

$$x_{\text{NO}_x \text{ into } \text{N}_2, T}(\%) = \left(1 - \frac{n_{\text{NO}, T} + n_{\text{NO}_2, T} + 2 n_{\text{N}_2\text{O}, T}}{n_{\text{NO}, 0} + n_{\text{NO}_2, 0}} \right) \times 100\% \quad (2)$$

$$x_{\text{NO}_x \text{ into } \text{N}_2\text{O}, T}(\%) = \frac{2 n_{\text{N}_2\text{O}, T}}{n_{\text{NO}, 0} + n_{\text{NO}_2, 0}} \times 100\% \quad (3)$$

$$x_{\text{CH}_4 \text{ into } \text{CO}_x, T}(\%) = \frac{n_{\text{CO}_2, T} + n_{\text{CO}, T}}{n_{\text{CH}_4, 0}} \times 100\% \quad (4)$$

$$\begin{aligned} S_{\text{CH}_4 \text{ to } \text{SCR}, T}(\%) &= \frac{n_{\text{CH}_4 \text{ for } \text{SCR}, T}}{n_{\text{CH}_4 \text{ converted}, T}} \\ &= \frac{1}{2} \frac{n_{\text{NO}, 0} + n_{\text{NO}_2, 0} - (n_{\text{NO}, T} + n_{\text{NO}_2, T} + 2 n_{\text{N}_2\text{O}, T})}{n_{\text{CH}_4, 0} - (n_{\text{CO}_2, T} + n_{\text{CO}, T})} \times 100\% \end{aligned} \quad (5)$$

O 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 CH₄-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 CeO₂ species are stabilized and less CeO₂ species in interaction with Pd are present in the catalyst, which results in a lower CH₄ selectivity towards SCR.

Acknowledgments

The authors acknowledge Fundação para a Ciência e a Tecnologia (FCT)—project UID/QUI/00100/2013 and grant SFRH/BD/78639/2011—and ENGIE for financial support (Project ENGIE/IST/UPMC).

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

1. European Environment Agency. *Nec Directive Status Report 2013*; European Environment Agency: Luxembourg, 2014.
2. Granger, P.; Parvulescu, V.I. Catalytic NO_x abatement systems for mobile sources: From three-way to lean burn after-treatment technologies. *Chem. Rev.* **2011**, *111*, 3155–3207.
3. Liu, G.; Gao, P.X. A review of NO_x storage/reduction catalysts: Mechanism, materials and degradation studies. *Catal. Sci. Technol.* **2011**, *1*, 552–568.
4. Iwasaki, M.; Shinjoh, H. A comparative study of “standard”, “fast” and “NO₂” SCR reactions over Fe/zeolite catalyst. *Appl. Catal. A* **2010**, *390*, 71–77.
5. Armor, J.N. Catalytic reduction of nitrogen-oxides with methane in the presence of excess oxygen—A review. *Catal. Today* **1995**, *26*, 147–158.

6. Ferreira, A.P.; Capela, S.; da Costa, P.; Henriques, C.; Ribeiro, M.F.; Ribeiro, F.R. CH₄-SCR of NO over Co and Pd ferrierite catalysts: Effect of preparation on catalytic performance. *Catal. Today* **2007**, *119*, 156–165.
7. Decolatti, H.; Solt, H.; Lonyi, F.; Valyon, J.; Miro, E.; Gutierrez, L. The role of Pd-In interactions on the performance of PdIn-Hmordenite in the SCR of NO_x with CH₄. *Catal. Today* **2011**, *172*, 124–131.
8. Sobalik, Z. Abatement of NO_x and N₂O using zeolite catalysts. In *New and Future Developments in Catalysis: Catalysis for Remediation and Environmental Concerns*; Suib, S.L., Ed.; Elsevier: Amsterdam, The Netherlands, 2013; pp. 155–194.
9. Pieterse, J.A.Z.; Booneveld, S. Catalytic reduction of NO, with H₂/CO/CH₄ over PdMOR catalysts. *Appl. Catal. B* **2007**, *73*, 327–335.
10. Costilla, I.O.; Sanchez, M.D.; Alicia Volpe, M.; Gigola, C.E. Ce effect on the selective catalytic reduction of NO with CH₄ on Pd-mordenite in the presence of O₂ and H₂O. *Catal. Today* **2011**, *172*, 84–89.
11. Mendes, A.N.; Zholobenko, V.L.; Thibault-Starzyk, F.; da Costa, P.; Henriques, C. On the enhancing effect of Ce in Pd-MOR catalysts for NO_x CH₄-SCR: A structure-reactivity study. *J. Catal.* **2015**, submitted.
12. Homeyer, S.T.; Sachtler, W.M.H. Oxidative redispersion of palladium and formation of PdO particles in NaY—An application of high-precision TPR. *Appl. Catal.* **1989**, *54*, 189–202.
13. Adelman, B.J.; Sachtler, W.M.H. The effect of zeolitic protons on NO_x reduction over Pd/ZSM-5 catalysts. *Appl. Catal. B* **1997**, *14*, 1–11.
14. Reifsnnyder, S.N.; Otten, M.M.; Lamb, H.H. Nucleation and growth of Pd clusters in mordenite. *Catal. Today* **1998**, *39*, 317–328.
15. Alayon, E.M.; Nachtegaal, M.; Ranocchiari, M.; van Bokhoven, J.A. Catalytic conversion of methane to methanol over Cu-mordenite. *Chem. Commun.* **2012**, *48*, 404–406.
16. Wen, B.; Sun, Q.; Sachtler, W.M.H. Function of Pd⁰_n clusters, Pd²⁺(oxo-) ions, and Pdo clusters in the catalytic reduction of NO with methane over Pd/MFI catalysts. *J. Catal.* **2001**, *204*, 314–323.
17. De Oliveira, A.M.; Costilla, I.; Gigola, C.; Baibich, I.M.; da Silva, V.T.; Pergher, S.B.C. Characterization of Pd-mordenite catalysts for NO decomposition. *Catal. Lett.* **2010**, *136*, 185–191.
18. Shimizu, K.; Okada, F.; Nakamura, Y.; Satsuma, A.; Hattori, T. Mechanism of NO reduction by CH₄ in the presence of O₂ over Pd-H-mordenite. *J. Catal.* **2000**, *195*, 151–160.
19. Mortier, W.J. *Compilation of Extra Framework Sites in Zeolites*; Butterworth Scientific Limited: Surrey, UK, 1982.
20. Kaucky, D.; Vondrova, A.; Dedecek, J.; Wichterlova, B. Activity of Co ion sites in ZSM-5, ferrierite, and mordenite in selective catalytic reduction of NO with methane. *J. Catal.* **2000**, *194*, 318–329.
21. Marques, R.; Mazri, L.; da Costa, S.; Delacroix, F.; Djega-Mariadassou, G.; da Costa, P. Selective reduction of NO_x by hydrogen and methane in natural gas stationary sources over alumina-supported Pd, Co and Co/Pd catalysts—Part A. On the effect of palladium precursors and catalyst pre-treatment. *Catal. Today* **2008**, *137*, 179–184.
22. Trovarelli, A. Catalytic properties of ceria and CeO₂-containing materials. *Catal. Rev.* **1996**, *38*, 439–520.

23. Cordoba, L.F.; Flytzani-Stephanopoulos, M.; de Correa, C.M. Lean NO_x reduction with dodecane over cerium and palladium loaded mordenite. *Appl. Catal. B* **2001**, *33*, 25–33.
24. Li, Z.J.; Flytzani-Stephanopoulos, M. On the promotion of Ag-ZSM-5 by cerium for the SCR of NO by methane. *J. Catal.* **1999**, *182*, 313–327.
25. Gaspar, A.B.; Dieguez, L.C. Dispersion stability and methylcyclopentane hydrogenolysis in Pd/Al₂O₃ catalysts. *Appl. Catal. A* **2000**, *201*, 241–251.
26. Marques, R.; Mazri, L.; da Costa, S.; Delacroix, F.; Djega-Mariadassou, G.; da Costa, P. Selective reduction of NO_x by hydrogen and methane in natural gas stationary sources over alumina supported Pd, Co and Co/Pd catalysts—Part B: On the effect of bimetallic catalyst preparation. *Catal. Today* **2008**, *137*, 185–190.
27. Gelin, P.; Primet, M. Complete oxidation of methane at low temperature over noble metal based catalysts: A review. *Appl. Catal. B* **2002**, *39*, 1–37.
28. Li, Y.J.; Armor, J.N. Catalytic combustion of methane over palladium exchanged zeolites. *Appl. Catal. B* **1994**, *3*, 275–282.
29. Descorme, C.; Gélín, P.; Lécuyer, C.; Primet, M. Catalytic reduction of nitric oxide by methane in the presence of oxygen on palladium-exchanged mordenite zeolites. *J. Catal.* **1998**, *177*, 352–362.

© 2015 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).