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## Accepted Manuscript

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**On the enhancing effect of Ce in Pd-MOR catalysts for NO<sub>x</sub> CH<sub>4</sub>-SCR: a structure-reactivity study**

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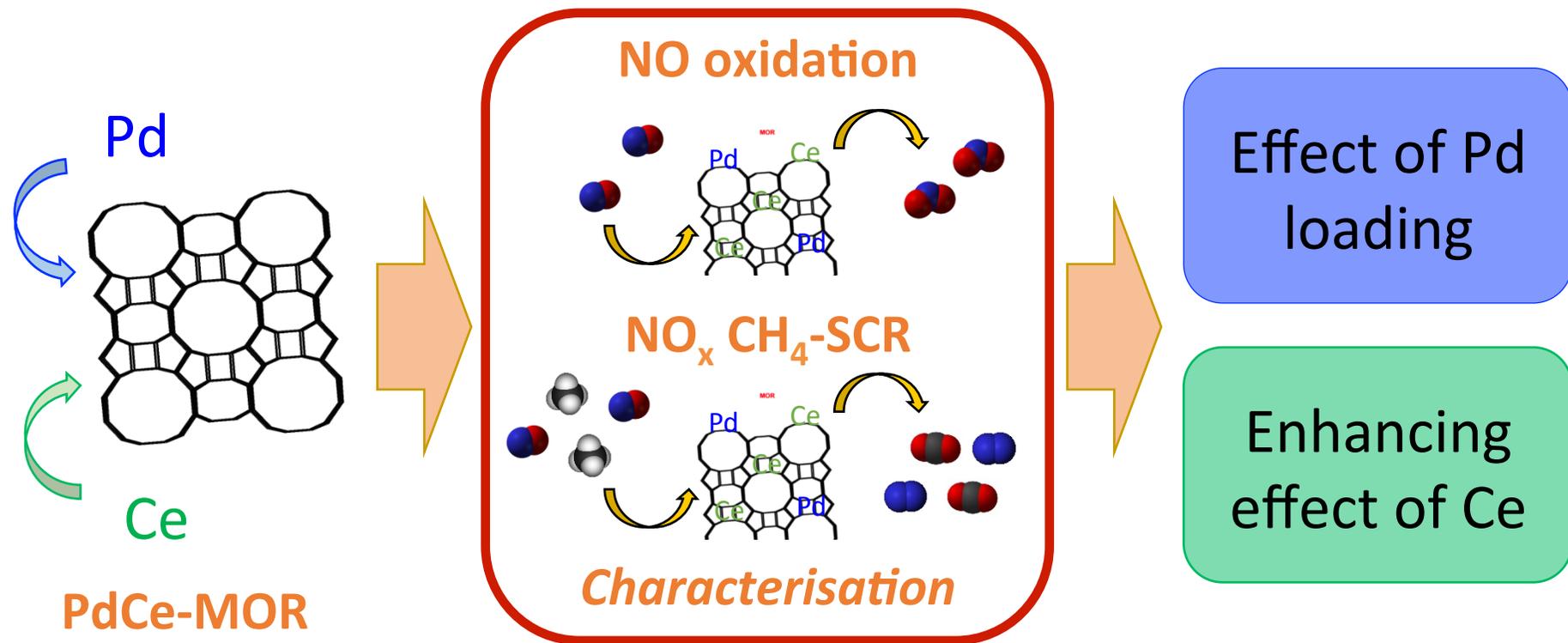
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**Graphical abstract**

## structure/reactivity study



**Highlights**

- This study is focused on PdCe-HMOR as a catalyst for NO<sub>x</sub> CH<sub>4</sub>-SCR reaction.
- Evidence of Pd<sup>2+</sup> ions stabilised in two different positions of MOR is provided.
- For the Pd-MOR, N<sub>2</sub>O formation instead of N<sub>2</sub> is favoured above 0.3 wt.% of Pd.
- The presence of CeO<sub>2</sub> species interacting with Pd<sup>2+</sup> enhances catalytic performance

## Abstract

The effect of palladium and cerium species on the selective catalytic reduction (SCR) of  $\text{NO}_x$  using methane as reductant ( $\text{NO}_x$   $\text{CH}_4$ -SCR) has been investigated using Pd-HMOR and PdCe-HMOR system. The catalysts have been characterised by  $\text{H}_2$ -TPR, DRS UV-Vis, TEM/EDS and FTIR using CO and pyridine as probe molecules. The oxidation of NO and  $\text{CH}_4$ -SCR catalytic tests have been conducted using monometallic and bimetallic formulations.

Above 0.3 wt.% Pd, the increase in Pd loading leads to a decrease in  $\text{NO}_x$  selectivity towards  $\text{N}_2$ , with the formation of  $\text{N}_2\text{O}$ , and a decrease in the  $\text{CH}_4$  selectivity towards SCR, due to  $\text{CH}_4$  direct combustion.  $\text{H}_2$ -TPR and FTIR-CO studies indicate that palladium is stabilised as  $\text{Pd}^{2+}$  in ion-exchange position, probably in two different sites within the MOR framework.

The addition of cerium to Pd-HMOR enhances its catalytic performance for  $\text{NO}_x$   $\text{CH}_4$ -SCR. With 1 wt.% Ce, both  $\text{NO}_x$  conversion into  $\text{N}_2$  and  $\text{CH}_4$  selectivity towards SCR have increased. Small  $\text{CeO}_2$  clusters interacting with palladium are likely to play a major role in this catalytic reaction. The number of such species increases up to Ce loading of *ca.* 2 wt.%. However, above 3 wt%,  $\text{NO}_x$  conversion values decrease with Ce loading, which is attributed to the formation of bulk  $\text{CeO}_2$  species not interacting with palladium.

Keywords:  $\text{NO}_x$  HC-SCR, methane, MOR, palladium, cerium.

## 1. Introduction

Over the recent decades, many countries devoted considerable resources to mitigating the impact of air pollution. Nitrogen oxides (NO<sub>x</sub>) are one of the pollutants associated with air pollution and road transportation sector is known to be one of the major contributors to the NO<sub>x</sub> emissions. In 2012 this sector was responsible for about 31% of the total emissions of NO<sub>x</sub> in the European Union (EU), more than 10.7 Mton [1]. Several directives have been published over the years by the EU imposing increasingly tough restrictions on NO<sub>x</sub> emissions. The most recent directive, known as EURO 6 standard, came into force on 1<sup>st</sup> September 2014 for the approval of vehicles, and from 1<sup>st</sup> January 2015 for the registration and sale of new types of cars, imposing a drastic reduction on NO<sub>x</sub> emissions for heavy-duty and light passenger compression ignition engines (see Table 1).

Table 1 – HC and NO<sub>x</sub> emissions for heavy-duty and light passengers vehicles, from Euro 1 to Euro 6 standards [2].

	Heavy-duty		Light passengers (compression ignition)		Light passengers (positive ignition)		
	HC (g/kWh)	NO <sub>x</sub> (g/kWh)	HC+NO <sub>x</sub> (g/km)	NO <sub>x</sub> (g/km)	HC (g/km)	HC+NO <sub>x</sub> (g/km)	NO <sub>x</sub> (g/km)
Euro 1 (1992)	1.1	8	0.97	-	-	0.97	-
Euro 2 (1996)	1.1	7	0.7	-	-	0.5	-
Euro 3 (2000)	0.66	5	0.56	0.5	0.2	-	0.15
Euro 4 (2005)	0.46	3.5	0.3	0.25	0.1	-	0.08
Euro 5 (2009)	0.46	2	0.23	0.18	0.1	-	0.06
Euro 6 (2014)	0.13	0.4	0.17	0.08	0.1	-	0.06

Highly effective systems based on the so-called “3-way” catalysts have been successfully used by the automotive industry in order to simultaneously eliminate the harmful emissions (NO<sub>x</sub>, CO and unburned hydrocarbons – HC) from vehicle engines that work in stoichiometric air-to-fuel ratio (positive ignition engines, typically for gasoline vehicles) [3]. However, for lean-burn engines, which work in excess of oxygen (compression ignition

engines, typically diesel vehicles), this technology is not effective for eliminating NO<sub>x</sub> emissions.

A promising technology that has been developed to address this issue is the selective catalytic reduction of NO<sub>x</sub> with hydrocarbons (HC-SCR) [3, 4]. This technology aims to use unburned hydrocarbons contained in the exhaust gases as reductant in order to reduce NO<sub>x</sub> to N<sub>2</sub>, leading to the simultaneous removal of NO<sub>x</sub> and HC, which appears to be particularly suitable for natural gas powered vehicles (NGVs). It is expected that the number of NGVs would significantly increase in the coming years. According to the NGV Global Association, the number of NGVs worldwide has increased from about 7.4 million (2007) to 16.7 million (2012) [5]. For these reasons, the continuous study of after-treatment systems capable of mitigating the pollution from these vehicles, namely NO<sub>x</sub> emissions, is pertinent and necessary.

For NGVs, the most abundant hydrocarbon in the exhaust gases is CH<sub>4</sub>. Zeolite-based catalysts containing different metals have been reported as active materials for the selective catalytic reduction of NO<sub>x</sub> with methane (CH<sub>4</sub>-SCR). Cobalt-containing zeolites, introduced by Li and Armor as active catalysts for CH<sub>4</sub>-SCR [6], have been widely studied by the scientific community [7-11]. This research has significantly contributed to the understanding of the nature of active species involved in this reaction, as well as the important parameters that influence NO<sub>x</sub> CH<sub>4</sub>-SCR reaction, such as, temperature, [CH<sub>4</sub>]/[NO] feed ratio, water feed content, *etc.* It is known that the use of bimetallic formulations leads to a better catalytic performance. Many studies on bimetallic zeolite-based catalysts have been conducted, including Pd/Co [12-18], Pt/Co [19, 20], In/Co [21-23], La/Co [24], Zn/Co [25], Ag/Co [26] and Mn/Co [27]. However, the use of Co in final products such as catalytic converters may be restricted for legal reasons. Many compounds, including cobalt (II) chloride, carbonate, acetate, nitrate and sulphate are chemical products which are included in the candidate list of

substances of very high concern for authorisation (REACH regulation) [28]. Some of these, namely cobalt (II) diacetate and cobalt (II) dinitrate, are commonly used in the preparation of Co-zeolite catalysts. Though their use is not forbidden, the EU suppliers of products that contain these substances in a concentration above 0.1 wt.% need to declare it to the appropriate authorities, which may discourage companies to invest in the development of this type of technology.

Zeolites-based catalysts containing metals other than Co are also claimed to be active in CH<sub>4</sub>-SCR. Nishizaka and Mizono [29] published the first report describing Pd-zeolites as active catalysts in this reaction. Since then, several studies have been conducted in order to move forward to a better understanding of this system. As in the case of the Co-based systems, the use of a second metal in the Pd-based catalyst to enhance its performance has been widely reported, *e.g.* Pd/Pt [30], Pd/In [31, 32], and Pd/Ce [33-35] systems.

Compared to platinum and indium, the use of cerium may represent an advantage from the economical point of view. Promising results for Pd/Ce system have been presented already [34, 35]; however, the role of various Pd and Ce species in the NO<sub>x</sub> CH<sub>4</sub>-SCR requires further investigation. The aim of this work is to further understand the structure-reactivity relationship in the Pd/Ce zeolites, in particular the role of different metal species in the enhancement of their catalytic performance.

## 2. Experimental Part

### 2.1. Catalysts preparation

Catalysts were prepared from CBV21A zeolite (NH<sub>4</sub>MOR), with Si/Al = 10 supplied by Zeolyst International. Monometallic Pd-zeolites were obtained from by NH<sub>4</sub>MOR by ion-exchanging the zeolite with [Pd(NH<sub>3</sub>)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub> aqueous solutions of adequate concentration, at room temperature, for 24 h. In a typical preparation, 6 g of the parent zeolite was mixed under stirring with 300 mL of a Pd complex solution (*e.g.* 0.15 wt.% prepared by dilution of the original 10 wt.% aqueous solution of [Pd(NH<sub>3</sub>)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub>, Sigma-Aldrich, 99.99%). The ion-exchanged samples were recovered by centrifugation and dried overnight at 90°C. Next, Pd-zeolites were calcined under air flow at 500°C for 1 h (1°C/min temperature ramp). Bimetallic PdCe-zeolites were obtained from Pd(0.3)-HMOR, by incipient wetness impregnation, using solutions of adequate concentration prepared from Ce(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O (Fluka, 99% purity). Samples were dried overnight at 90°C and finally calcined at 500°C for 8 h (5°C/min temperature ramp). Monometallic Ce(2)-HMOR was obtained from NH<sub>4</sub>MOR, following the same procedure as previously described. HMOR form was prepared from NH<sub>4</sub>MOR via calcination at 500°C, for 8 h (5°C/min temperature ramp). The chemical composition data for the catalysts investigated in this work are presented in Table 2.

Table 2 – Chemical composition of the catalysts obtained by ICP-OES analysis.

Catalyst**	Al (wt.%)	Pd (wt.%)	Ce (wt.%)	ER <sub>Pd</sub> * (%)	ER <sub>Ce</sub> * (%)
Pd(0.15)-HMOR	3.3	0.16	-	2.4	-
Pd(0.3)-HMOR	3.3	0.36	-	5.5	-
Pd(0.5)-HMOR	3.3	0.55	-	8.4	-
Pd(0.7)-HMOR	3.3	0.75	-	11.7	-
Pd(0.3)Ce(1)-HMOR	3.3	0.35	0.8	5.4	13.7
Pd(0.3)Ce(2)-HMOR	3.4	0.29	1.9	4.3	32.2
Pd(0.3)Ce(3)-HMOR	3.5	0.39	2.8	5.6	46.0
Pd(0.3)Ce(5)-HMOR	2.9	0.27	4.8	4.8	97.1
Pd(0.3)Ce(10)-HMOR	2.8	0.27	9.1	4.8	185.3
Ce(2)-HMOR	3.3	-	2.1	-	36.6

\*ER – Exchange rate (Assuming 2+ and 3+ charges for Pd and Ce, respectively).

\*\* Numbers in parentheses indicate theoretical wt.% of Pd and Ce.

## 2.2. Catalysts characterisation

Temperature programmed reduction under hydrogen ( $H_2$ -TPR) was performed by contacting a catalyst sample (*ca.* 100 mg) with a mixture of  $H_2$  (5 vol.%) / Ar and heating it up to 950°C using a ramp of 7.5°C/min. Hydrogen consumption was measured with a thermal conductivity detector. Water was removed using a dry ice cooled trap.

Diffuse reflectance UV-Vis spectroscopy (DRS UV-Vis) was performed using a *Varian Cary 5000 UV-Vis-NIR* spectrophotometer equipped with a *Praying Mantis* accessory. Spectra were collected at room temperature, using calcined samples (range 200-800 nm, scan rate of 600 nm/min, 1 nm data interval, SBW = 4 nm) and presented using the Schuster-Kubelka-Munk (SKM) function,  $F(R)$  – see 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 minimise the effect of zeolite framework absorption, a HMOR sample was used as standard.

Transmission electron microscopy (TEM) was performed on a *JEOL JEM 2010* microscope (LaB6 cannon) operating at 200 kV. Prior to TEM measurements, samples were crushed and then dispersed in ethanol and deposited onto a carbon-coated copper TEM grid. Energy-dispersive X-ray spectroscopy (EDS) was also performed (probe PGT-Bruker).

CO adsorption monitored by FTIR spectroscopy was performed in order to evaluate the state of Pd and Ce species. The spectra were collected using a Nicolet 6700 FTIR spectrometer equipped with a DTGS detector (400-4000  $cm^{-1}$ , 128 scans, 4  $cm^{-1}$  resolution). Self-supported wafers of the calcined catalysts (*ca.* 10  $mg/cm^2$ ) were pre-treated by heating to 400°C at 3°C/min, then holding for 30 min under vacuum ( $P < 10^{-5}$  torr, cell with  $CaF_2$  windows).

Next, samples were reduced at 400°C, for 1 h, under 100 torr of H<sub>2</sub>. After reduction, the cell was evacuated during 10 min to  $P < 10^{-5}$  torr. The wafers were then cooled down to room temperature and a spectrum was collected prior to CO adsorption. 5 torr of CO was introduced into the cell and the spectra of the sample and of the CO gas phase were collected. All spectra presented were obtained by subtracting the contributions from the CO gas phase and from the reduced sample, followed by normalisation to the same weight/surface area ratio of the wafer.

Pyridine adsorption and consecutive thermodesorption studies were monitored by *in situ* FTIR in order to quantify the acidity of the samples, utilising the same experimental apparatus and pre-treatment as that previously described for the CO adsorption experiments. After pre-treatment, the wafers were cooled down to room temperature and a spectrum was collected prior to pyridine adsorption. 1 torr of pyridine was introduced into the cell and spectra of the sample and the pyridine gas phase were collected. Then, the temperature was raised to 150°C, kept for 30 min, and another spectrum was collected. Next, the wafer was cooled down until room temperature and the cell was evacuated for 10 min ( $P < 10^{-5}$  torr). A spectrum was collected. Afterwards, the temperature was raised to 50°C, kept for 10 min, and a spectrum was collected. The same procedure was repeated every 50°C until 400°C. The quantification of total number of Brønsted acid sites (BAS) and Lewis acid sites (LAS) was performed through the integration of IR bands around 1545 and 1455 cm<sup>-1</sup>, respectively, using molar extinction coefficients reported elsewhere [36]. Although the data from reference [36] are frequently quoted in the literature, according to our AGIR studies [37], their use may lead to a significant overestimate of the concentration of acid sites since the sample mass was not monitored during the pyridine adsorption in reference [36].

### 2.3. Catalytic tests

Catalytic tests were performed in a tubular *pyrex* reactor using 190 mg of the catalyst (dry basis), supported by a sintered plate (frit). Prior to reaction studies, catalysts were heated under argon flow (15 L/h) to 500°C (5°C/min temperature ramp) and kept at this temperature for 1 h. Then, the reactor was cooled to 300°C whilst the reaction mixture was stabilised in the reactor by-pass. Once stable, the reaction mixture was fed to the reactor. When steady-state conditions were reached, the temperature was raised by 50°C and the procedure was repeated up to the reaction temperature of 500°C.

NO<sub>x</sub> SCR tests were performed using a mixture of 1000 ppm NO, 1000 ppm CH<sub>4</sub> and 7 vol.% O<sub>2</sub> in flowing argon (total flow rate of 15 L/h, GHSV = 40000 h<sup>-1</sup>). Oxidation of NO to NO<sub>2</sub> was performed under similar conditions, but using a mixture of 1000 ppm NO and 7 vol.% O<sub>2</sub> in flowing argon.

The reactor outlet flow was continuously analysed using a Thermo 42C chemiluminescence detector for measuring the concentrations of NO and NO<sub>2</sub>, an ABB EL 3020 infrared analyser to monitor CO, CO<sub>2</sub> and N<sub>2</sub>O concentrations and a Pfeiffer Vacuum GSD 301 mass spectrometer to follow the concentration of CH<sub>4</sub> (m/z = 15).

For each temperature,  $T$ , NO<sub>x</sub> conversion into N<sub>2</sub> was obtained using Equation (2), CH<sub>4</sub> conversion into CO<sub>2</sub> was obtained using Equation (3) and selectivity of methane to SCR reaction was obtained using equation (4).

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

$$x_{CH_4 \text{ into } CO_2, T}(\%) = \frac{n_{CO_2, T}}{n_{CH_4, 0}} \times 100\% \quad (3)$$

$$S_{CH_4 \text{ to } SCR, T}(\%) = \frac{n_{CH_4 \text{ for } SCR, T}}{n_{CH_4 \text{ converted}, T}} = \frac{1 n_{NO, 0} + n_{NO_2, 0} - (n_{NO, T} + n_{NO_2, T} + 2 n_{N_2O, T})}{n_{CH_4, 0} - (n_{CO_2, T} + n_{CO, T})} \times 100\% \quad (4)$$

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

### 3. Results and discussion

#### 3.1. Effect of Pd loading

##### 3.1.1. Temperature Programmed Reduction under H<sub>2</sub>

H<sub>2</sub>-TPR profiles of HMOR and Pd(x)-HMOR catalysts (with x = 0.15, 0.3, 0.5 and 0.7 wt.% Pd) are presented in Figure 1. A single peak found between 80-180°C can be ascribed to Pd<sup>2+</sup> ions in exchange position [38-40]. The integration of this peak for each sample yields a H<sub>2</sub>/Pd ratio close to unity, suggesting that all Pd is stabilised as Pd<sup>2+</sup>.

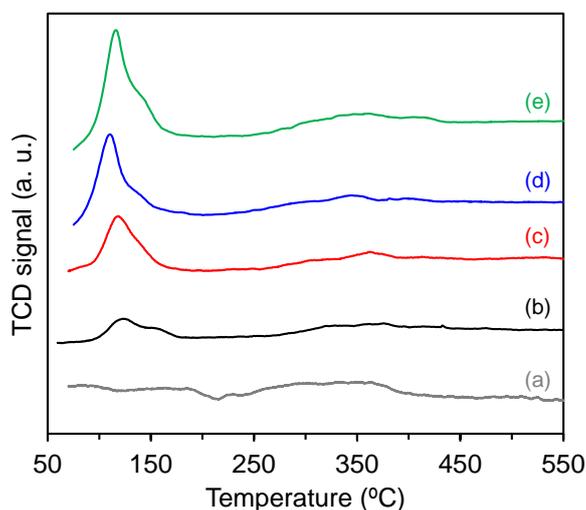


Figure 1 – H<sub>2</sub>-TPR profile of Pd-HMOR catalysts with different Pd loadings: HMOR (a), Pd(0.15)-HMOR (b), Pd(0.3)-HMOR (c), Pd(0.5)-HMOR (d) and Pd(0.7)-HMOR (e).

Further analysis of the H<sub>2</sub>-TPR profiles in the region between 80-180°C (Figure 2) reveals two Gaussian components of the reduction peak: the first centred at temperatures below 125°C and the second above 130°C. One possible explanation for this phenomenon might be the stabilisation of Pd<sup>2+</sup> ions in different exchange positions of the MOR structure. Dedecek and Wichterlová conducted a detailed investigation of the nature of Co<sup>2+</sup> ions and their occupancy in mordenite, using DRS UV-Vis-NIR spectroscopy [41]. By studying Co-MOR samples, containing different amounts of Co introduced by ion-exchange, they identified three

different Co species ( $\alpha$ ,  $\beta$  and  $\gamma$ ), corresponding to different three different spectral components of DRS-UV-Vis-NIR spectrum. These different  $\text{Co}^{2+}$  ions would be stabilised in specific ion-exchange sites corresponding, respectively to sites E, A and C according the nomenclature proposed by Mortier [42].

A density functional investigation conducted by Grybos *et al.* [43] focused on the stabilisation of  $\text{Pd}^{2+}$  ions in mordenite exchange positions corresponding to sites A, B, C, D and E proposed by Mortier [42]. The authors studied the role of Al distribution over the zeolite framework and concluded that, despite being more or less random, it has an effect on the stability of  $\text{Pd}^{2+}$  ions in each site, which is related to the number of bonds between Pd and O atoms directly connected to Al sites. Based on the calculation of the total energy associated to each configuration for Al ions distribution involved in the different sites, the authors concluded that, though Pd location in positions B, D and E do not represent a very large penalty in terms of total energy, positions A and C are the energetically most favourable locations for  $\text{Pd}^{2+}$  cations [43].

In the present work, it is not possible to describe the nature and location of different  $\text{Pd}^{2+}$  ions with the same degree of precision. Nevertheless, for each sample, the integration of the two Gaussian peaks allows to estimate the distribution of palladium as two different  $\text{Pd}^{2+}$  ions (Figure 2, Table 3), although their exact location (for instance, 12-membered ring channels and side pockets) cannot be identified. The fraction of each of the species stabilised in the zeolite framework is almost constant (approximately 70% / 30%) for all Pd loadings, resulting from a proportional increase in the concentration of both species at higher Pd loading. It should be noted that even at 0.7 wt.% of Pd, the exchange rate is relatively low (11.7%), meaning that only a small amount of exchange positions are occupied by  $\text{Pd}^{2+}$  ions.

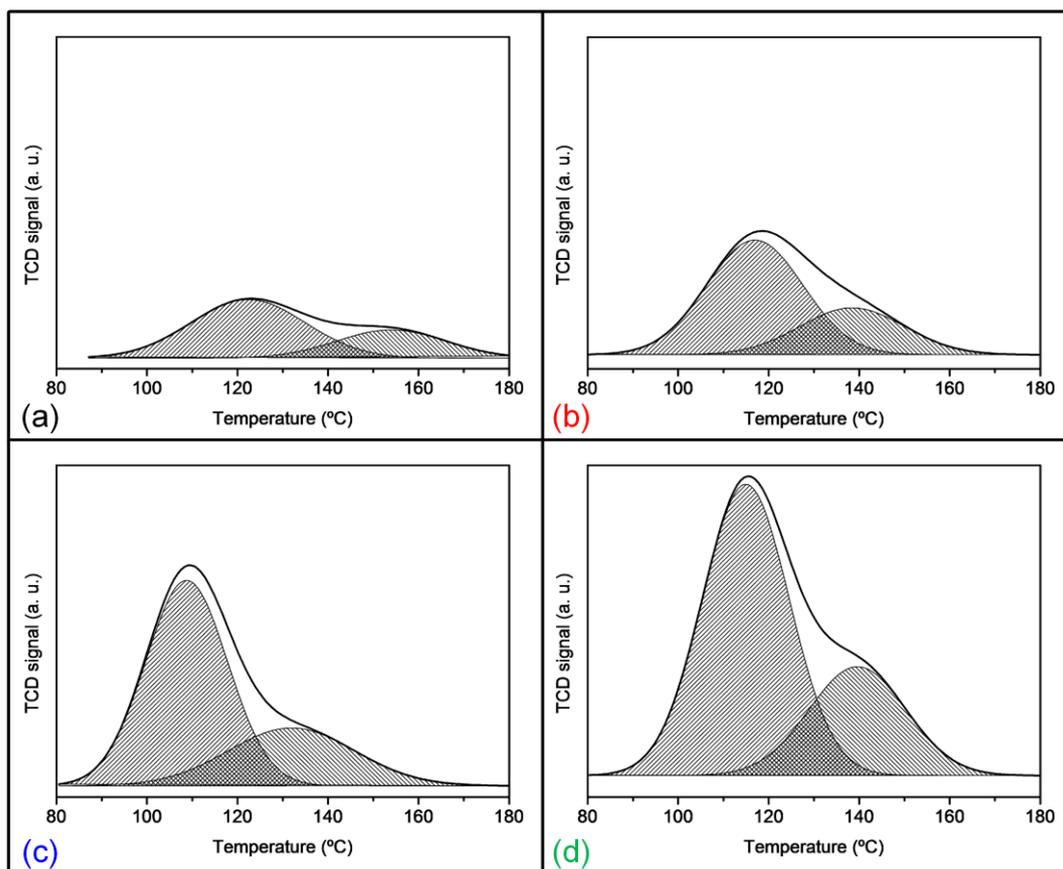


Figure 2 – Gaussian peak fitting to  $H_2$ -TPR profiles of Pd(0.15)-HMOR (a), Pd(0.3)-HMOR (b), Pd(0.5)-HMOR (c) and Pd(0.7)-HMOR (d).

Table 3 – Quantification of the relative amount of  $Pd^{2+}$  corresponding to both reduction processes of Pd(x)-HMOR ( $x = 0.15, 0.3, 0.5$  and  $0.7$ ) from Figure 2.

	Gaussian peak A		Gaussian peak B	
	T (°C)	Amount of $Pd^{2+}$	T (°C)	Amount of $Pd^{2+}$
Pd(0.15)-HMOR	121	68%	153	32%
Pd(0.3)-HMOR	118	69%	141	31%
Pd(0.5)-HMOR	109	70%	132	30%
Pd(0.7)-HMOR	114	71%	136	29%

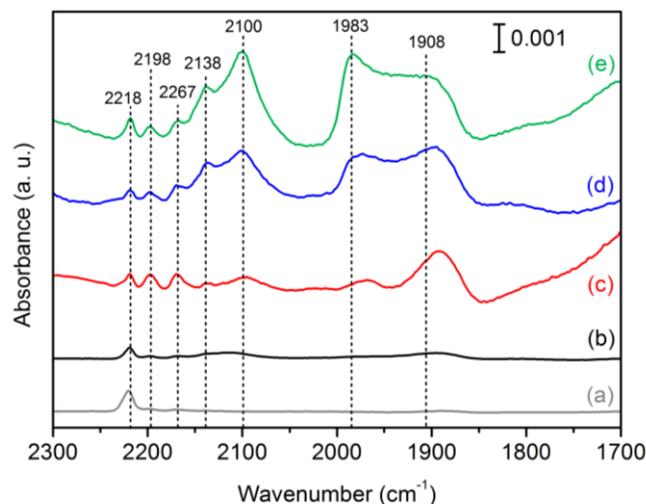
3.1.2. CO adsorption followed by FTIR spectroscopy

Figure 3 – FTIR spectra of reduced catalysts collected at room temperature, after exposure to 5 torr of CO: HMOR (a), Pd(0.15)-HMOR (b), Pd(0.3)-HMOR (c), Pd(0.5)-HMOR (d) and Pd(0.7)-HMCOR (e).

Figure 3 presents the FTIR spectra of HMOR and Pd(x)-HMOR catalysts after CO adsorption. In the spectrum of HMOR sample, two bands observed at  $\sim 2220$  and  $\sim 2199$   $\text{cm}^{-1}$  can be assigned to  $\text{Al}^{3+}$ -CO complexes resulting from the interaction of CO with extra-framework Al [44-46]. These bands are also observed for all Pd(x)-HMOR catalysts.

For Pd(x)-HMOR samples, three additional groups of bands are observed between 2220 and 1890  $\text{cm}^{-1}$ . According to Hadjiivanov and Vayssilov [44], IR bands in the 2215-2110  $\text{cm}^{-1}$  spectral range have been attributed to linear  $\text{Pd}^{\text{n}+}$ -CO complexes. The band at  $\sim 2167$   $\text{cm}^{-1}$  can be assigned to residual Pd cations, such as  $\text{Pd}^{2+}$  [44], or to Brønsted acid sites (BAS) [31, 38], whereas the band at 2140  $\text{cm}^{-1}$  can be ascribed to  $\text{Pd}^+$ -CO or  $\text{Pd}^{\delta+}$ -CO complexes [38]. The presence of both bands suggests the existence of Pd cations or small positively charged Pd clusters, likely to be located in the vicinity of BAS, even after reduction in  $\text{H}_2$  at 400°C. Bands below  $\sim 2100$   $\text{cm}^{-1}$  are typical of CO interactions with metallic palladium species [44]. The bands at 2114-2100  $\text{cm}^{-1}$  are assigned to linear  $\text{Pd}^0$ -CO complexes, which appear slightly blue-shifted for Pd(0.15)-HMOR and Pd(0.3)-HMOR. The bands between 1983 and 1892

$\text{cm}^{-1}$  are attributed to bridging CO on  $\text{Pd}^0$  clusters (two-fold and three-fold co-ordinations, the latter are found below  $\sim 1900 \text{ cm}^{-1}$ ). The low intensity of all these bands in Pd(0.15)-HMOR can be related to the low palladium content in the sample. For Pd(0.3)-HMOR, Pd(0.5)-HMOR and Pd(0.7)-HMOR catalysts, the intensity of the bands typical for  $\text{Pd}^0$ -CO complexes is significantly increased reflecting the higher contents of palladium in these samples and a higher degree of reduction to metallic palladium species. The bands attributed to bridging CO complexes on  $\text{Pd}^0$  are blue-shifted for Pd(0.5)-HMOR and Pd(0.7)-HMOR, probably due to the larger Pd particle size (Figure 3), which corresponds to the fact that these species are more stable in these catalysts.

### 3.1.3. Active species on Pd-HMOR for $\text{NO}_x$ $\text{CH}_4$ -SCR

The catalytic performance of Pd(x)-HMOR catalysts for  $\text{NO}_x$   $\text{CH}_4$ -SCR was assessed at the reaction temperatures between 300 and 500°C (Figure 4). Pd(0.15)-HMOR presents slightly lower  $\text{NO}_x$  conversion values than the other catalysts, whereas for Pd loadings between 0.3-0.7 wt.%, all catalysts present similar values of  $\text{NO}_x$  and  $\text{CH}_4$  conversion, with practically no formation of  $\text{N}_2\text{O}$ . However, at 500°C, a decrease in  $\text{NO}_x$  conversion to  $\text{N}_2$  is observed as the Pd loading increases from 0.3 to 0.7 wt.%, accompanied by an increase in both  $\text{N}_2\text{O}$  formation and  $\text{CH}_4$  conversion.  $\text{NO}_x$  selectivity to  $\text{N}_2$ , which is almost 100 % for Pd(0.15)-HMOR, is decreasing with the increase of Pd loading (Figure 4d).

The best catalytic performance can be achieved by maximising both  $\text{NO}_x$  total conversion and  $\text{NO}_x$  selectivity to  $\text{N}_2$ . However, these two parameters evolve in opposite directions, when Pd loading is increased. At 500°C, total  $\text{NO}_x$  conversion has increased with Pd loading, but  $\text{N}_2\text{O}$  formation is being promoted instead of  $\text{N}_2$ . In fact, above 0.3 wt.% Pd, catalysts present lower  $\text{NO}_x$  conversion in  $\text{N}_2$  than Pd(0.3)-HMOR. On the other hand, though Pd(0.15)-HMOR

presents a very high  $\text{NO}_x$  selectivity to  $\text{N}_2$ , the conversion is considerably lower when compared, for instance, with Pd(0.3)-HMOR. Based on these data, one can suggest that the 0.3 wt.% Pd loading corresponds to the optimal loading.

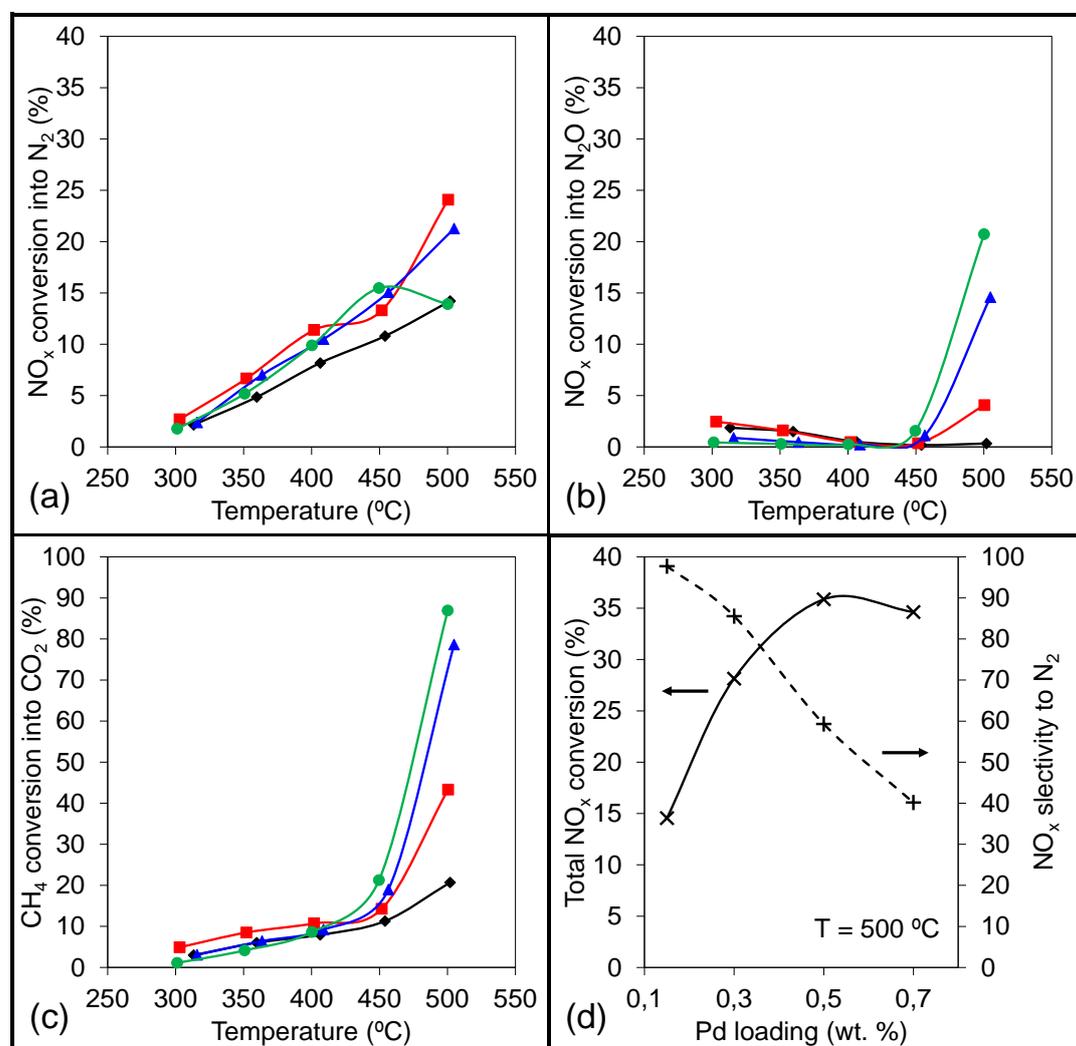


Figure 4 – $\text{NO}_x$   $\text{CH}_4$ -SCR catalytic test results for Pd(0.15)-HMOR (◆), Pd(0.3)-HMOR (■), Pd(0.5)-HMOR (▲) and Pd(0.7)-HMOR (●):  $\text{NO}_x$  conversion into  $\text{N}_2$  (a) and into  $\text{N}_2\text{O}$  (b),  $\text{CH}_4$  conversion into  $\text{CO}_2$  (c), and total  $\text{NO}_x$  conversion and  $\text{NO}_x$  selectivity to  $\text{N}_2$  as function of Pd loading (d). Conditions: 1000 ppm  $\text{NO}$ , 1000 ppm  $\text{CH}_4$ , 7 vol.%  $\text{O}_2$  and GHSV of  $40000 \text{ h}^{-1}$ .

$\text{Pd}^{2+}$  ions have been identified in previous studies as active species for  $\text{NO}_x$   $\text{CH}_4$ -SCR in different Pd-based catalysts. For instance, Marques *et al.* [47] concluded that  $\text{Pd}^{2+}$  surrounded by oxygen atoms is the active site for de $\text{NO}_x$  process using methane as reductant and Pd on alumina as the catalysts. The same conclusion was made for bimetallic formulations, *e.g.*

Pd/Co-alumina [48]. Characterisation data presented herein for Pd-MOR catalysts indicate that palladium is dispersed as Pd<sup>2+</sup> in two different ion-exchange positions. The distribution of Pd<sup>2+</sup> between these two sites appears to be independent of the Pd loading. It is likely that these two types of cations would interact differently with the reactants, and therefore, would have different reactivity. Indeed, Kaucký *et al.* [49] concluded that cobalt cations located in different positions of the MOR and FER zeolites have different activity for NO<sub>x</sub> CH<sub>4</sub>-SCR.

Palladium-loaded catalysts are also used as hydrocarbon oxidation catalysts [50, 51] and the direct combustion of CH<sub>4</sub> is increasing with Pd loading, which has been also confirmed in this work (Figure 4c). However, this increase in CH<sub>4</sub> conversion is often associated with the presence of PdO species, which is not the case for the catalysts studied in this work. Instead, one of the Pd<sup>2+</sup> species may play a role in CH<sub>4</sub> combustion. One of these species may be involved in the formation of N<sub>2</sub>O and in the direct combustion of CH<sub>4</sub>. Descorme, *et al.* [52] have presented evidences for the existence of two different nitrosyl complexes formed with Pd cations in different locations of MOR zeolite. Pd mononitrosyl complexes located in the main channels of MOR would be responsible for the NO<sub>x</sub> SCR activity, whereas Pd dinitrosyl complexes formed in the side pocket of MOR would be inactive in this reaction. Though no evidence pointed at involvement of Pd located in side pockets in the N<sub>2</sub>O formation or CH<sub>4</sub> combustion, one cannot exclude this possibility in the light of the results herein presented.

### 3.2. The enhancing effect of cerium

#### 3.2.1. Temperature programmed reduction under $H_2$ ( $H_2$ -TPR)

Three groups of reduction peaks have been identified in  $H_2$ -TPR profiles of Pd(0.3)Ce(x)-HMOR (Figure 5): (i) between  $\sim 70$  and  $220$ , (ii)  $\sim 225$  and  $560$  and (iii)  $\sim 560$  and  $920^\circ\text{C}$ . As for Pd(x)-HMOR, the first peak, attributed to the reduction of  $\text{Pd}^{2+}$  cations in different exchange positions, consists of two components, one centred at  $\sim 120^\circ\text{C}$  and the other close to  $150^\circ\text{C}$ . As the Ce loading increases, the second component becomes more prominent and appears to shift to higher temperatures. For samples with the Ce content over 2 wt.%, the integration of the peaks in the region  $70$ - $220^\circ\text{C}$  yields the  $H_2/\text{Pd}$  ratio greater than one. This can be explained by the presence of surface  $\text{Ce}^{4+}$  species, which are reduced in this temperature range [53].

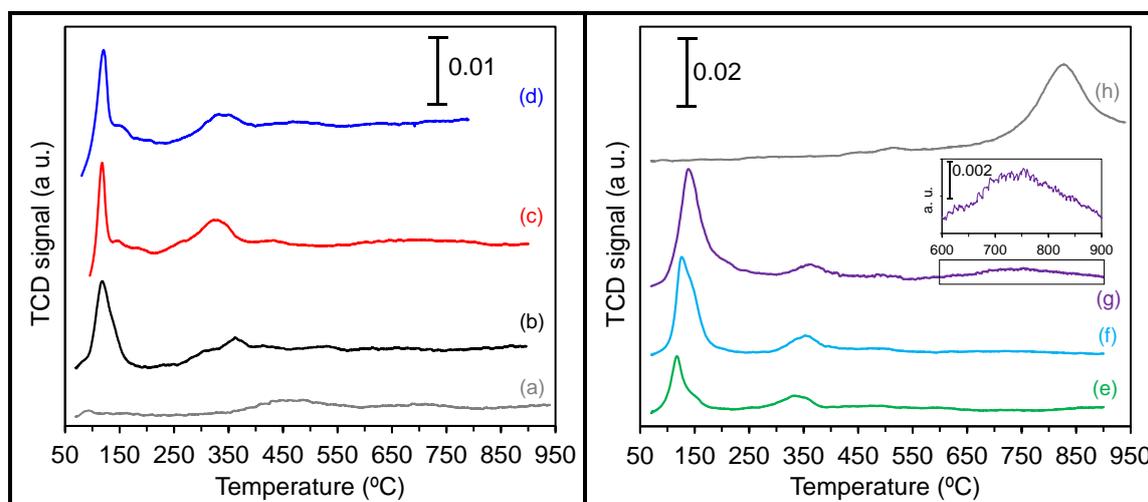


Figure 5 –  $H_2$ -TPR profile of PdCe-HMOR catalysts with different Ce loadings: Ce(2)-HMOR (a), Pd(0.3)-HMOR (b), Pd(0.3)Ce(1)-HMOR (c), Pd(0.3)Ce(2)-HMOR (d), Pd(0.3)Ce(3)-HMOR (e), Pd(0.3)Ce(5)-HMOR (f), Pd(0.3)Ce(10)-HMOR (g) and  $\text{CeO}_2/\text{HMOR}$  (h)

Table 4 – Peak integration of H<sub>2</sub>-TPR profiles of Pd(0.3)Ce(x)-HMOR (x = 1, 2, 3, 5 and 10).

	Peak 1			Peak 2			Peak 3		
	T (°C)	H <sub>2</sub> /Pd	$\mu\text{mol H}_2$ /g <sub>catal.</sub>	T (°C)	H <sub>2</sub> /Ce	$\mu\text{mol H}_2$ /g <sub>catal.</sub>	T (°C)	H <sub>2</sub> /Ce	$\mu\text{mol H}_2$ /g <sub>catal.</sub>
Pd(0.3)Ce(1)-HMOR	100-210	1.0	32	250-560	0.39	22	-	-	-
Pd(0.3)Ce(2)-HMOR	95-215	1.4	39	240-560	0.27	37	-	-	-
Pd(0.3)Ce(3)-HMOR	70-220	1.4	50	225-560	0.14	29	-	-	-
Pd(0.3)Ce(5)-HMOR	75-220	4.1	103	250-560	0.10	35	-	-	-
Pd(0.3)Ce(10)-HMOR	70-270	6.0	152	290-560	0.02	15	560-920	0.06	41

The second reduction peak can be identified between ~225-560°C in all catalysts containing Ce. This peak is attributed to the reduction of CeO<sub>2</sub> species interacting with Pd [54]. This interaction between species is typical for ceria, which is known to form “bronzes” with noble metals, namely with Pd [53].

An additional broad reduction peak is observed in the TPR profile of Pd(0.3)Ce(10)-HMOR at 560-920°C. This peak is attributed to the reduction of bulk CeO<sub>2</sub> [53]. For this sample, the existence of higher amounts of CeO<sub>2</sub> species can be explained by the very high loading of Ce. A broad reduction peak corresponding to this species can be clearly observed in the reduction profile of CeO<sub>2</sub>/HMOR sample, obtained by mechanical mixture of bulk CeO<sub>2</sub> with HMOR zeolite in proportion 1:2.

### 3.2.2. Diffuse reflectance UV-Vis spectroscopy (DRS UV-Vis)

DRS UV-Vis spectra of the Pd(0.3)-HMOR and Pd(0.3)Ce(x)-HMOR (x = 1, 2, 3, 5 and 10) are presented in Figure 6. For the bimetallic catalysts, two bands between 250 and 300 nm can be attributed to cerium species: the first band, at 260 nm, corresponds to the 4f-5d transition in Ce<sup>3+</sup> [55, 56], and the second band, at 290 nm, is characteristic of the charge transfer from

$O^{2-}$  to  $Ce^{4+}$  in  $CeO_2$  clusters [56]. The intensity of both bands increases with Ce loading. Furthermore, the increase in the Ce loading causes a blue-shift in the band around 400 nm attributed to the  $Pd^{2+}$  species, which might result from the interaction between Pd and Ce species that has also been observed in  $H_2$ -TPR. For Ce loadings above 5 wt.%, the bands corresponding to Ce species become so intense that it is no longer possible to clearly observe the band around 400 nm.

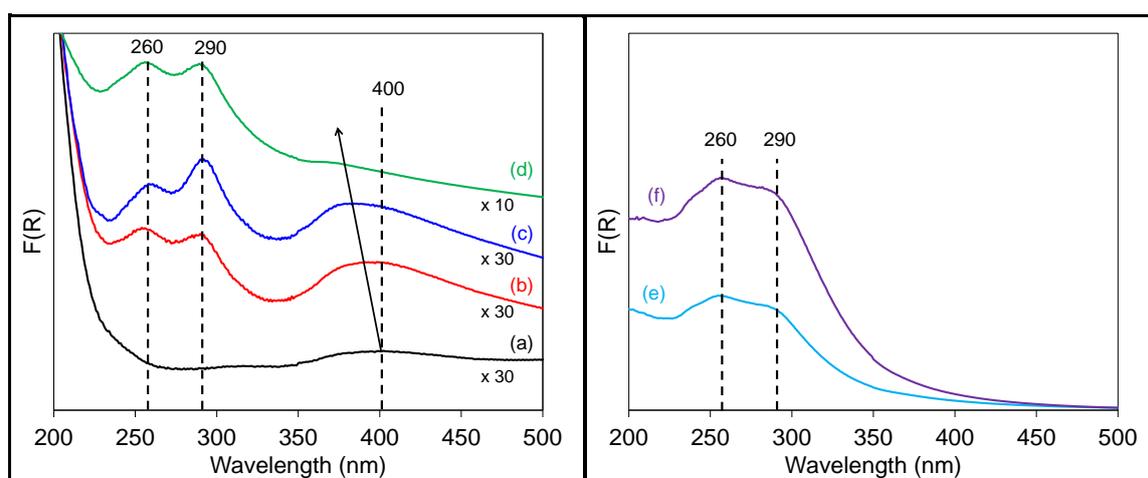


Figure 6 – DRS UV-Vis spectra of PdCe-HMOR catalysts containing 0.3 wt.% of Pd and different loadings of Ce: Pd(0.3)-HMOR (a), Pd(0.3)Ce(1)-HMOR (b), Pd(0.3)Ce(2)-HMOR (c), Pd(0.3)Ce(3)-HMOR (d), Pd(0.3)Ce(5)-HMOR (e) and Pd(0.3)Ce(10)-HMOR (f).

### 3.2.3. Transmission electron microscopy (TEM/EDS)

TEM images for Pd(0.3)-HMOR, Ce(2)-HMOR and Pd(0.3)Ce(2)-HMOR are presented in Figure 7. For Pd(0.3)-HMOR, no metal particles are observed in the TEM images collected (Figure 7a,b). Additionally, energy-dispersive X-ray spectroscopy (EDS) analyses do not detect palladium in the sample. The detection limit of this technique does not allow to detect low amounts of Pd in samples where it is well dispersed.

For Ce(2)-HMOR, several Ce-containing clusters can be observed in TEM images (Figure 7c). These clusters have irregular shapes, their estimated size (~10 nm) is about one order of magnitude smaller than the zeolite particle size (~100 nm). High resolution TEM and EDS analyses confirm these are CeO<sub>2</sub> clusters with the lattice d-spacing of 2.7 and 3.1 Å (ICDD 00-034-0394). Similar CeO<sub>2</sub> clusters have been observed in Pd(0.3)Ce(2)-HMOR and Ce(2)-HMOR, but no Pd particles have been identified indicating a high degree of palladium dispersion in the zeolite framework after cerium introduction.

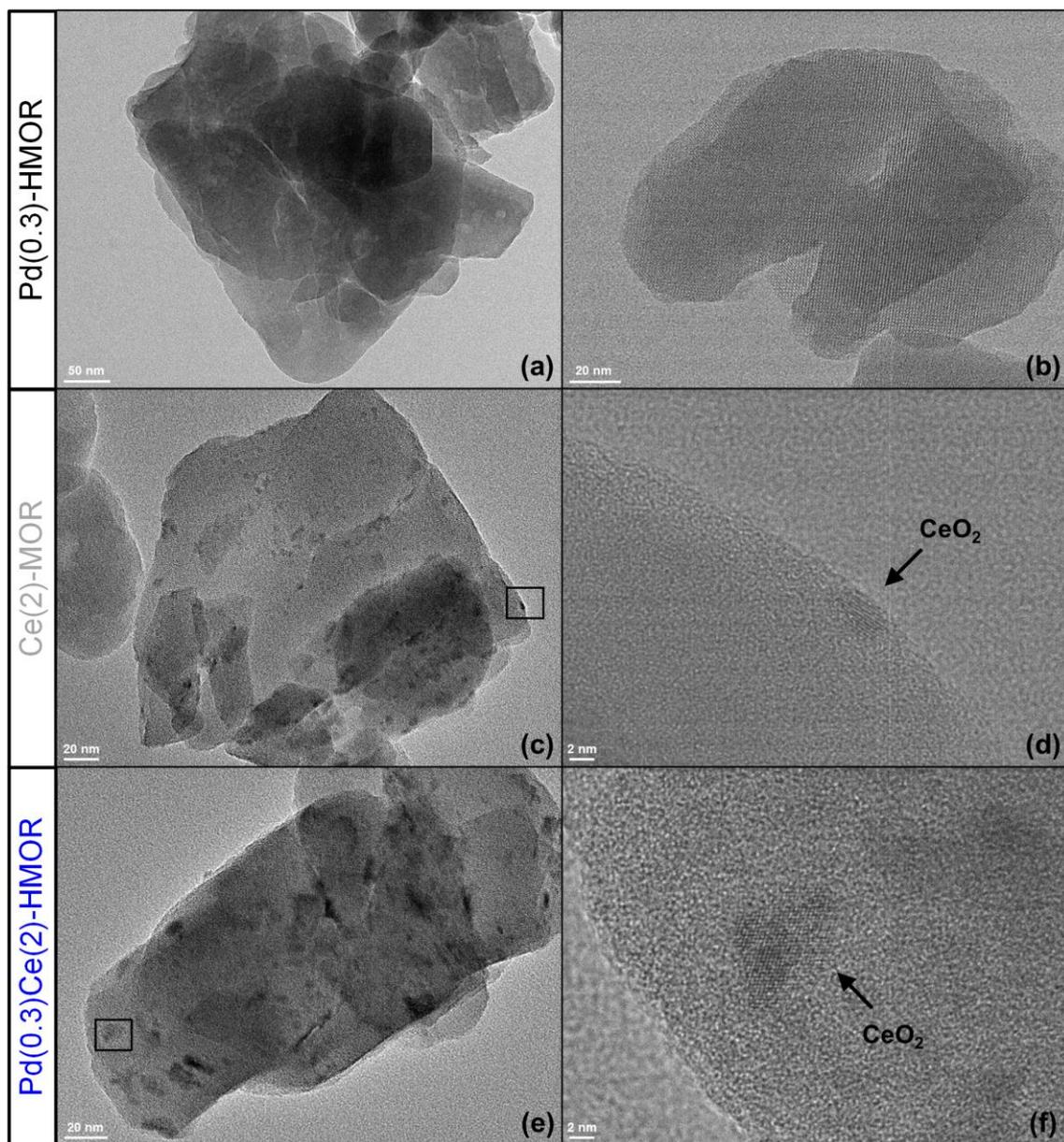


Figure 7. TEM images: Pd(0.3)-HMOR (a, b), Ce(2)-HMOR(c, d) and Pd(0.3)Ce(2)-HMOR (e, f).

## Quantification of acid sites by pyridine-FTIR spectroscopy

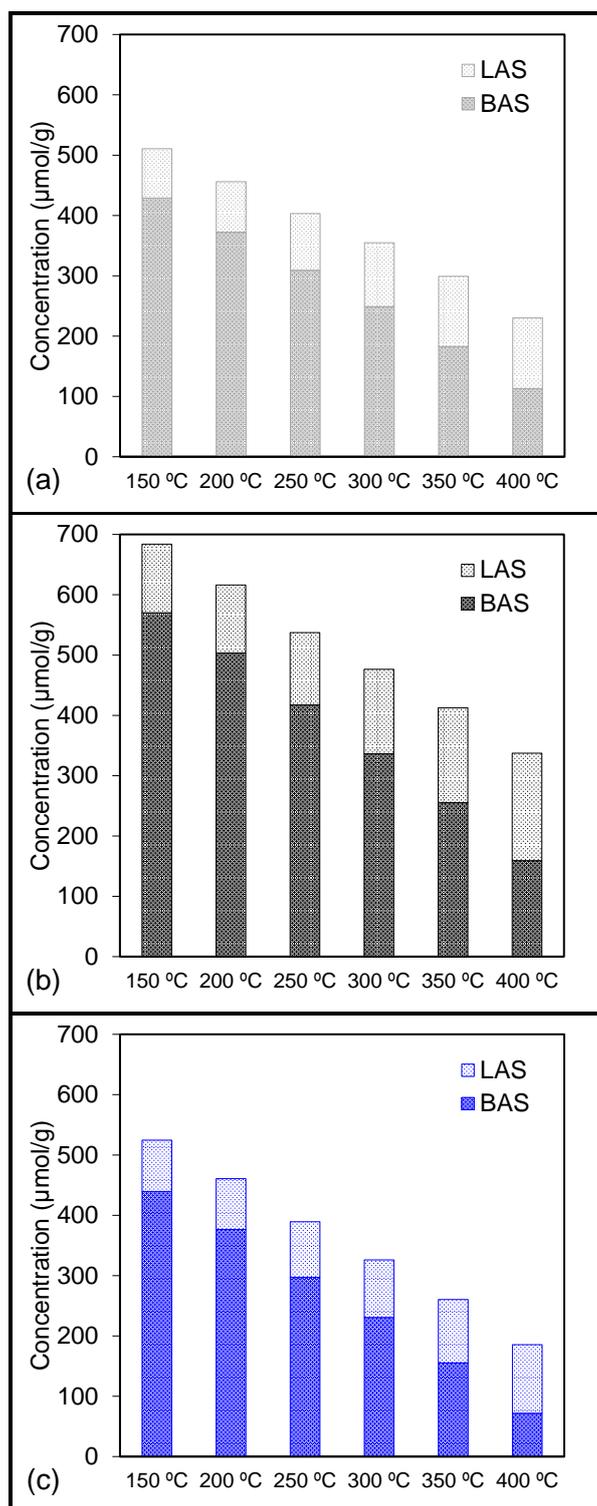


Figure 8 – Quantification of acid sites of HMOR (a), Pd(0.3)-HMOR (b) and Pd(0.3)Ce(2)-HMOR (c) using pyridine thermodesorption followed by FTIR.

The role of zeolite Brønsted acid sites (BAS) in  $\text{NO}_x$   $\text{CH}_4$ -SCR has been widely studied and reported in literature [40, 57-59]. The results of acidity measurements carried out in this work are presented in Figure 8. The data show that Pd(0.3)-HMOR has a significantly higher number of BAS ( $503 \mu\text{mol/g}$ ,  $200^\circ\text{C}$ ) as compared to both HMOR ( $372 \mu\text{mol/g}$ ,  $200^\circ\text{C}$ ) and Pd(0.3)Ce(2)-HMOR ( $377 \mu\text{mol/g}$ ,  $200^\circ\text{C}$ ). This could be related to partial dihydroxylation or restricted access of pyridine to acid sites resulted from the calcination of the latter two samples at  $500^\circ\text{C}$  for an extended period of time. As the maximum rate of  $\text{Pd}^{2+}$  exchange in Pd(0.3)Ce(2)-HMOR is below 4% (Table 2), it should not significantly affect the number of BAS. In contrast, if a considerable part of cerium was stabilised as  $\text{Ce}^{3+}$  during ion exchange, one would expect a significant decrease on acidity, since the maximum exchange rate of Ce in Pd(0.3)Ce(2)-HMOR is around 30%. The fact that HMOR and Pd(0.3)Ce(2)-HMOR present similar values of BAS indirectly confirms that  $\text{Ce}^{3+}$  ions are not the predominant Ce species stabilised in the zeolite matrix. Indeed, according to the TEM data,  $\text{CeO}_2$  is formed during the catalysts preparation and high temperature treatment.

#### 3.2.4. CO adsorption followed by FTIR spectroscopy

FTIR spectra of CO adsorbed on HMOR, Pd(0.3)-HMOR, Pd(0.3)Ce(2)-HMOR and Ce(2)-HMOR are compared in Figure 9. In the spectra of Pd(0.3)Ce(2)-HMOR and Ce(2)-HMOR an intense band is observed at  $2188 \text{ cm}^{-1}$  that can be attributed to  $\text{Ce}^{n+}$ -CO complexes ( $\text{Ce}^{3+}$  or  $\text{Ce}^{4+}$ ) [44], which have been previously identified by DRS UV-Vis spectroscopy. An additional band is also observed at  $2123 \text{ cm}^{-1}$ , which has not been found in Pd(0.3)-HMOR and Ce(2)-HMOR. This band can be assigned to either  $\text{Ce}^{n+}$ -CO or  $\text{Pd}^{n+}$ -CO species ( $2215$ - $2110 \text{ cm}^{-1}$  spectral range) not present in the monometallic catalysts.

The band at  $2290\text{ cm}^{-1}$  is ascribed to  $\text{CO}_2$  complexes formed due to CO oxidation, it appears together with an intense band at  $2355\text{ cm}^{-1}$  attributed to linear  $\text{CO}_2$  [60] (not shown). These bands only appear in the bimetallic catalyst, which suggests that CO oxidation seems to require the presence of both Pd and Ce species. The band at  $\sim 1888\text{ cm}^{-1}$  is probably related to the formation of carbonate species.

The bands at  $2141$ ,  $2101$ ,  $1959$  and  $1894\text{ cm}^{-1}$  in Pd(0.3)-HMOR can be attributed to CO adsorbed on the Pd species previously described for monometallic PdMOR samples.

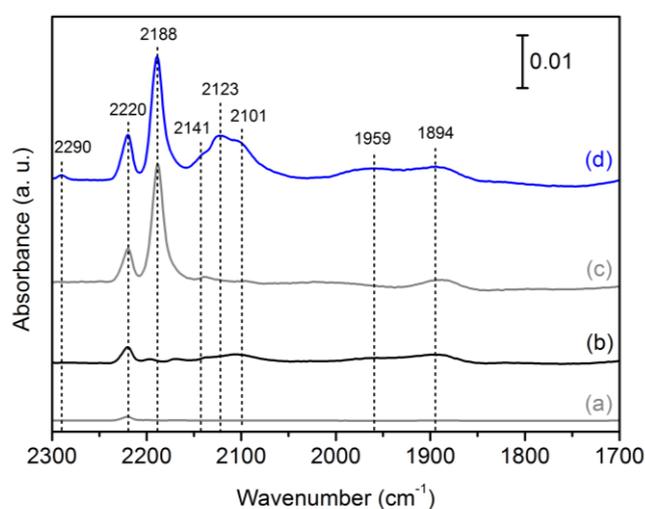


Figure 9 – FTIR spectra of reduced catalysts at room temperature, after CO exposure to 5 torr: HMOR (a), Pd(0.3)-HMOR (b), Ce(2)-HMOR (c) and Pd(0.3)Ce(2)-HMOR (d).

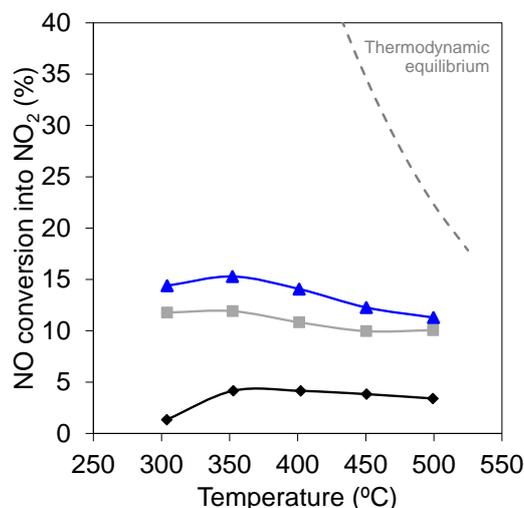
3.2.5. NO oxidation

Figure 10 – Conversion of NO into NO<sub>2</sub> for Pd(0.3)-HMOR (◆), Ce(2)-HMOR (■) and Pd(0.3)Ce(2)-HMOR (▲). Conditions: 1000 ppm NO, 7 vol.% O<sub>2</sub> and GHSV of 40000 h<sup>-1</sup>.

Oxidation of NO to NO<sub>2</sub> is considered to be the first key step in the NO<sub>x</sub> SCR reaction involving hydrocarbons as reducing agents [61-63]. Figure 10 shows conversion of NO into NO<sub>2</sub> as a function of temperature in the absence of methane (the hydrocarbon reducing agent). The oxidation activity increases in the order Pd(0.3)-HMOR < Ce(2)-HMOR < Pd(0.3)Ce(2)-HMOR. This suggests that Ce species play a role in promoting NO conversion over Pd(0.3)Ce(2)-HMOR and could also act to enhance the catalytic performance of this catalyst in NO<sub>x</sub> CH<sub>4</sub>-SCR by oxidising NO to NO<sub>2</sub> [34].

The role of Ce as oxidation promoter has also been confirmed by FTIR-CO, as the formation of CO<sub>2</sub> complexes on Pd(0.3)Ce(2)-HMOR, resulting from the CO oxidation, has been detected in the infrared spectra. However, this phenomenon has not been observed for the monometallic formulations.

### 3.2.6. Active species in Pd/Ce-HMOR for NO<sub>x</sub> CH<sub>4</sub>-SCR

The enhancing effect of Ce on NO<sub>x</sub> CH<sub>4</sub>-SCR has been assessed by testing the Pd(0.3)Ce(x)-HMOR catalysts in comparison to Pd(0.3)-HMOR and Ce(2)-HMOR (Figure 11; N<sub>2</sub>O and CO formation is negligible and is not presented).

Ce(2)-HMOR is practically inactive in the NO<sub>x</sub> CH<sub>4</sub>-SCR reaction up to 450°C. Even at 500°C, NO<sub>x</sub> conversion value is only 6%, which is significantly lower than for Pd(0.3)-HMOR (24%). At lower temperatures, 300-350°C, all Pd-based catalysts present similar NO<sub>x</sub> and CH<sub>4</sub> conversion. However above 350°C, the addition 1-5 wt.% Ce leads to an increase in NO<sub>x</sub> conversion. For Ce loadings of 1 and 2 wt.%, NO<sub>x</sub> conversion increases with the reaction temperature, whereas for 3 and 5 wt.% loadings, maximum NO<sub>x</sub> conversion is reached at 450°C. This behaviour can be explained by the lack of CH<sub>4</sub>, since its conversion is over 80 % at 500°C.

An important indicator of the catalyst performance is its efficiency in using CH<sub>4</sub> to reduce NO<sub>x</sub>. When 1 wt.% Ce is added to Pd(0.3)-HMOR, the selectivity of methane to SCR reaction increases. For higher Ce loadings, the selectivity becomes lower than that for Pd(0.3)-HMOR; however, there is also a significant difference in the NO<sub>x</sub> conversion to N<sub>2</sub>.

The catalytic behaviour of the catalyst with the highest Ce content, Pd(0.3)Ce(10)-HMOR, changes considerably: both the NO<sub>x</sub> and CH<sub>4</sub> conversions decrease, probably because Ce-containing species are poorly dispersed in the zeolite structure. Indeed, the NO<sub>x</sub> conversion is similar for Pd(0.3)Ce(10)-HMOR and Pd(0.3)-HMOR that was mechanically mixed with bulk CeO<sub>2</sub> in order to obtain a similar Ce loading in the sample, *ca.* 10 wt.% - Pd(0.3)Ce(10)-HMOR(MM), for which one would expect a low cerium dispersion with larger CeO<sub>2</sub> particles present on the external surface of the zeolite (Figure 12). H<sub>2</sub>-TPR profile of Pd(0.3)Ce(10)-

HMOR(MM) is presented in the supplementary data showing the reduction of bulk  $\text{CeO}_2$  at high temperature.

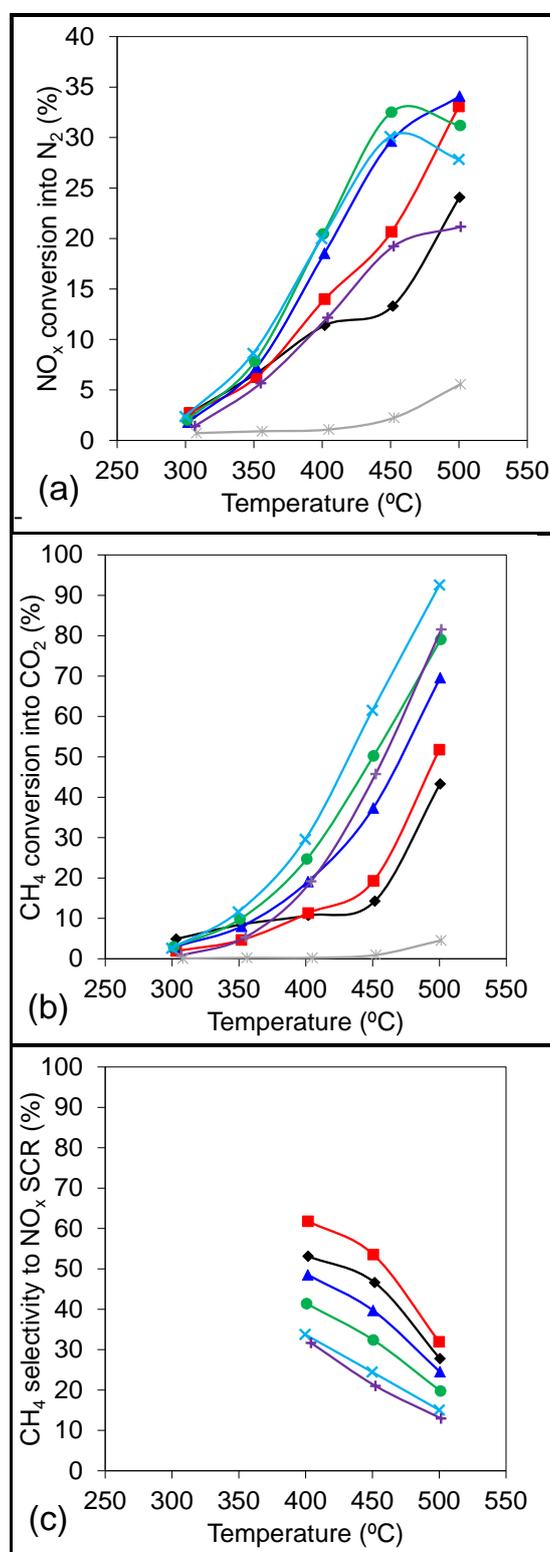


Figure 11 – NO<sub>x</sub> CH<sub>4</sub>-SCR catalytic test results for Pd(0.3)-HMOR (◆), Pd(0.3)Ce(1)-HMOR (■), Pd(0.3)Ce(2)-HMOR (▲), Pd(0.3)Ce(3)-HMOR (●), Pd(0.3)Ce(5)-HMOR (x), Pd(0.3)Ce(10)-HMOR (+) and Ce(2)-

HMOR(\*): NO<sub>x</sub> conversion into N<sub>2</sub> (a), CH<sub>4</sub> conversion into CO<sub>2</sub> (b) and CH<sub>4</sub> selectivity to NO<sub>x</sub> SCR reaction (c). Conditions: 1000 ppm NO, 1000 ppm CH<sub>4</sub>, 7% O<sub>2</sub> and GHSV of 40000 h<sup>-1</sup>.

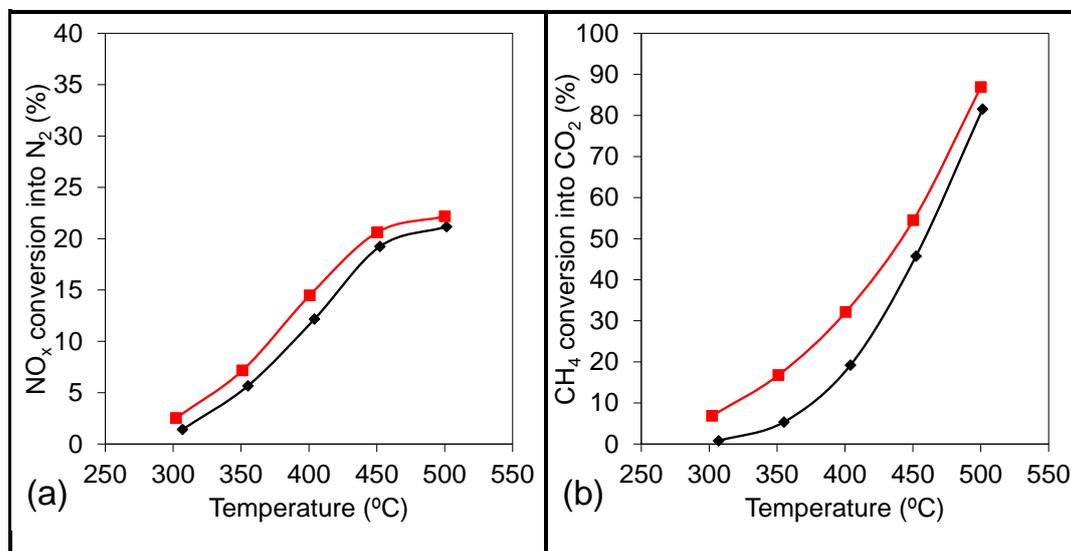


Figure 12 – NO<sub>x</sub> CH<sub>4</sub>-SCR catalytic test results for Pd(0.3)Ce(10)-HMOR(IWI) (◆) and Pd(0.3)Ce(10)-HMOR(MM) (■): NO<sub>x</sub> conversion into N<sub>2</sub> (a) and CH<sub>4</sub> conversion into CO<sub>2</sub> (b). Conditions: 1000 ppm NO, 1000 ppm CH<sub>4</sub>, 7% O<sub>2</sub> and GHSV of 40000 h<sup>-1</sup>:

Although Ce(2)-HMOR is practically inactive in NO<sub>x</sub> CH<sub>4</sub>-SCR reaction and in the direct combustion of methane, this catalyst shows moderate conversion values for NO oxidation to NO<sub>2</sub>, which are higher than those for Pd(0.3)-HMOR. Therefore, it can be suggested that the role of cerium species is to promote the oxidation of NO, which is in agreement with the data previously reported in the literature [34, 64]. Several mechanisms proposed for the HC-SCR reaction indicate that NO oxidation to NO<sub>2</sub> is the first key step in the HC-SCR reaction. This work provides important details regarding Ce species promoting NO oxidation over zeolite-based catalysts. TEM/EDS and H<sub>2</sub>-TPR indicate that these are well dispersed CeO<sub>2</sub> oxide clusters observed in the catalysts with a moderate Ce loading, *e.g.* Pd(0.3)Ce(2)-HMOR. H<sub>2</sub>-TPR, DRS UV-Vis and FTIR-CO also show that Pd and Ce species interact with each other, which might be the key for the promotion of deNO<sub>x</sub> process.

For Pd(0.3)Ce(x)-HMOR catalysts, the quantification of the second reduction peak in H<sub>2</sub>-TPR profiles results in a higher H<sub>2</sub>/Ce ratio for Pd(0.3)Ce(1)-HMOR, and the CH<sub>4</sub> selectivity towards SCR follows the same trend. The H<sub>2</sub>/Ce ratio corresponding to this reduction process can be seen as an indicator of the relative amount of cerium species interacting with palladium species, and the total amount of H<sub>2</sub> consumed in the reduction process is directly related to the absolute amount of Ce species interacting with Pd species. A decrease in the H<sub>2</sub>/Ce ratio with increasing Ce loading represents an increase in the number of Ce species not interacting with Pd, which would favour the direct combustion of methane.

The results suggest that the balance between the number of CeO<sub>2</sub> species interacting with Pd and those not interacting with it plays a crucial role in the catalytic performance of PdCe-HMOR in NO<sub>x</sub> CH<sub>4</sub>-SCR. For the catalyst containing 0.3 wt.% Pd and 2 wt.% Ce, the optimal Pd/Ce species distribution is obtained, resulting in the best catalytic performance in the SCR reaction studied in this work.

#### 4. Conclusions

The role of palladium and cerium species in the  $\text{NO}_x$   $\text{CH}_4$ -SCR reaction has been evaluated using mordenite catalysts containing Pd and Ce. These monometallic and bimetallic systems have been characterised by  $\text{H}_2$ -TPR, DRS UV-Vis, TEM/EDS, FTIR and their catalytic performance in NO oxidation and  $\text{CH}_4$ -SCR has been investigated.

The increase in palladium loading in Pd-HMOR leads to a decrease in  $\text{NO}_x$  selectivity towards  $\text{N}_2$ , favouring  $\text{N}_2\text{O}$  formation. The addition of cerium to Pd-HMOR enhances the catalytic performance for  $\text{NO}_x$   $\text{CH}_4$ -SCR. By adding 1 wt.% Ce, both  $\text{NO}_x$  conversion into  $\text{N}_2$  and  $\text{CH}_4$  selectivity towards SCR reaction are increased. However, for Ce loading above 3 wt.%, the direct combustion of methane is strongly favoured, in particular at high temperatures, resulting in a declining  $\text{NO}_x$   $\text{CH}_4$ -SCR performance.

$\text{Pd}^{2+}$  ions in exchange position are active species for de $\text{NO}_x$  process.  $\text{CeO}_2$  species play an important role in the NO oxidation to  $\text{NO}_2$ , which is considered as the first key step in the HC-SCR reaction. For PdCe-HMOR system, the existence of small  $\text{CeO}_2$  clusters interacting with Pd species leads to the enhanced catalytic performance. It appears that the balance between  $\text{CeO}_2$  species interacting with Pd and those which do not is an important parameter influencing the capacity of PdCe-HMOR catalysts to effectively use  $\text{CH}_4$  as the reducing agent in the de $\text{NO}_x$  process.

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