



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Contents lists available at ScienceDirect

Catalysis Today

journal homepage: [www.elsevier.com/locate/cattod](http://www.elsevier.com/locate/cattod)

# Ce effect on the selective catalytic reduction of NO with CH<sub>4</sub> on Pd-mordenite in the presence of O<sub>2</sub> and H<sub>2</sub>O

Ignacio O. Costilla<sup>a</sup>, Miguel D. Sanchez<sup>a,b</sup>, Maria Alicia Volpe<sup>a</sup>, Carlos E. Gigola<sup>a,\*</sup>

<sup>a</sup> Planta Piloto de Ingeniería Química (PLAPIQUI), Camino la Carrindanga Km 7, Bahía Blanca, 8000, Argentina

<sup>b</sup> Departamento de Física, Universidad Nacional del Sur (UNS), Av. Alem 1253, Bahía Blanca, 8000, Argentina

## ARTICLE INFO

### Article history:

Received 30 November 2010

Received in revised form 2 March 2011

Accepted 3 March 2011

Available online 9 April 2011

### Keywords:

Selective catalytic reduction of NO

Pd/H-MOR

Ce-Pd/H-MOR

FTIR

## ABSTRACT

The activity, selectivity and stability of Pd/H-MOR and Ce-Pd/H-MOR catalysts for the selective catalytic reduction of NO with CH<sub>4</sub> (SCR-CH<sub>4</sub>) were studied in O<sub>2</sub> excess (4.1%) in the absence and presence of H<sub>2</sub>O (5%). The reaction was carried out in a 300–650 °C temperature range with a S.V. of  $\cong 33,000 \text{ h}^{-1}$ . The characterization of fresh and used catalysts by FTIR spectroscopy of adsorbed CO and NO showed that the loss of NO conversion in H<sub>2</sub>O presence was due to a decreasing concentration of Pd<sup>2+</sup> sites and to the parallel formation of PdO particles that enhanced CH<sub>4</sub> combustion under dry conditions. This behavior was modified by Ce addition. Under wet conditions the Ce-Pd/H-MOR catalyst was very active ( $X_{\text{NO}} = 76\%$  at 550 °C), selective (100% of N<sub>2</sub>) and stable. The FTIR spectrum of CO adsorbed on used samples demonstrated that Ce inhibited the transformation of active Pd<sup>2+</sup> into PdO particles. However, Ce presence also enhanced CH<sub>4</sub> combustion under wet conditions. At low temperatures (<500 °C) H<sub>2</sub>O presence inhibited N<sub>2</sub>O formation and 90% selectivity to N<sub>2</sub>, which improved with Ce addition, was obtained.

© 2011 Published by Elsevier B.V.

## 1. Introduction

The selective catalytic reduction of NO<sub>x</sub> (SCR) in oxygen excess using hydrocarbons as reducing agents (SCR-HCs) is a technology that is still found in its development stage. In spite of the length of time elapsed from the first studies, an interest is kept in the utilization of CH<sub>4</sub> as reducing agent in order to replace NH<sub>3</sub>.

The discovery of the SCR-HCs of NO<sub>x</sub> in oxygen excess [1] involved the use of zeolites. The material studied most closely was ZSM-5 exchanged with copper. However, Cu/ZSM-5 catalyst is slightly active with methane. Nishizaka and Misono [2,3] and also Loughran and Resasco [4] demonstrated that low loadings of Pd supported on zeolitic materials gives place to a very selective catalyst for the SCR-CH<sub>4</sub> reaction, emphasizing clearly the importance of the acidity of the support material. Therefore, supports like H-MOR and SO<sub>4</sub>-ZrO<sub>2</sub> turn out to be appropriate to prepare Pd catalysts since they stabilize Pd<sup>2+</sup> species under reaction conditions [5,6]. Descorme et al. [7] analyzed the FTIR spectra of NO adsorbed on a Pd (0.98%)/H-MOR catalyst calcined at 500 °C. Due to high Pd loading, the catalyst contained particles of Pd and/or PdO besides Pd<sup>2+</sup> species. The study revealed the existence of different adsorption states: Pd mononitrosyl complexes at 1875 cm<sup>-1</sup>, which are

responsible for the catalytic activity, and Pd dinitrosyls located at 1908–1839 cm<sup>-1</sup> on Pd<sup>2+</sup>, which are inactive for SCR-CH<sub>4</sub>.

Shimizu et al. [8] studied the formation of species adsorbed under reaction conditions for a Pd (0.7%)/H-MOR catalyst, verifying the existence of NO–Pd<sup>2+</sup> at 1860 cm<sup>-1</sup>. It was observed that these species react with CH<sub>4</sub> and gives place to NH<sub>4</sub><sup>+</sup> formation on the acid sites of the zeolite support. According to the authors, the ammonium ion would react with the NO–Pd<sup>2+</sup> species to give N<sub>2</sub>. This reaction mechanism attributes a secondary role to NO<sub>2</sub>, which might also react with the ammonium ion to generate N<sub>2</sub>, and assigns similar importance to the Pd<sup>2+</sup> species and the acid sites of the H-MOR for SCR-CH<sub>4</sub>.

Unfortunately, the activity of metal-loaded zeolites decreases when the feed mixture contains water, as is the case with most combustion gases. Water induces the dealumination of the zeolites and the formation of PdO particles that enhances CH<sub>4</sub> combustion.

Ohtsuka and Tabata [9] found that Pd/H-MOR is more resistant to water than Pd/H-ZSM-5. Characterization of new and used catalysts by Raman spectroscopy demonstrated that H<sub>2</sub>O facilitates the agglomeration of Pd forming PdO crystals, which favor the combustion of CH<sub>4</sub>.

Different promoters have been used in order to improve the activity, selectivity and hydro-thermal stability of H-MOR supported Pd catalysts. In a relevant study [10] it was demonstrated that Ce incorporation to Pd-loaded H-MOR facilitates NO<sub>x</sub> reduction with dodecane in the presence of H<sub>2</sub>O and SO<sub>2</sub>. It has also been

\* Corresponding author.

E-mail address: [cgigola@plapiqui.edu.ar](mailto:cgigola@plapiqui.edu.ar) (C.E. Gigola).

reported by Pieterse et al. [11] that Ce incorporation to Pd/H-MOR catalysts increases the reduction of  $\text{NO}_x$  with  $\text{CH}_4$  under wet conditions. Apparently the promoter contributes to the stabilization of the active Pd species in the presence of  $\text{H}_2\text{O}$  because it limits the dealumination of the support material and/or Pd sintering. In a subsequent paper Pieterse et al. [12] demonstrated that the thermal stability of Pd/H-MOR catalysts for SCR- $\text{CH}_4$  is enhanced by the addition of rare earth oxides (undisclosed) up to  $400^\circ\text{C}$ . In this case, the feed mixture consisted of simulated and bona fide exhaust gases from a gas engine for the catalytic tests. However, the problem of dealumination and sintering was found to be significant above  $450^\circ\text{C}$ . More recently the beneficial effect of Ce on the activity, selectivity and stability of Pd/H-MOR catalysts for SCR was demonstrated again using gas mixtures containing  $\text{H}_2$  and CO [13]. Regarding the role of Ce, it was showed by TPR experiments that oxidized Pd species become more difficult to reduce.

Based on the previous studies, we have investigated the Ce effect on the activity and selectivity of a Pd/H-MOR catalyst of low metal content for the SCR- $\text{CH}_4$  reaction. The characterization of the preparations has been carried out by FTIR spectroscopy of adsorbed CO and NO on fresh and used samples, the attention being focused on the Pd phase. The activity and selectivity for SCR- $\text{CH}_4$  have been evaluated using an oxidizing mixture in the presence and absence of water.

## 2. Experimental

### 2.1. Catalyst preparation

The catalysts were prepared by using  $\text{NH}_4\text{-MOR}$  of Zeolyst ( $\text{SiO}_2/\text{Al}_2\text{O}_3$ :10,  $500\text{ m}^2/\text{g}$ ). Palladium was incorporated into the support by ion exchange with a solution ( $150\text{ cm}^3$ ) of  $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$  at  $\text{pH}=8$ . The incorporation of 3 g of  $\text{NH}_4\text{-MOR}$  to the solution decreased the pH to 6, but it was adjusted at 11 by the addition of a few drops of  $\text{NH}_3$  solution. The palladium solution was prepared with a concentration that was adequate to obtain a catalyst with a metal content close to 0.2%. The mixture was stirred for 8 h at room temperature to make the ion exchange possible. Next, the excess solution was removed and the solid was filtered, washed with deionized water and dried at  $120^\circ\text{C}$  for 4 h. Then, the preparation was calcined at  $400^\circ\text{C}$  under an air flow for 1.5 h in order to remove  $\text{NH}_4^+$  ions and to obtain the zeolite's protonic form.

A Ce-Pd/H-MOR catalyst that contained 2.0% Ce, was prepared by using an aqueous solution of ammonium cerium nitrate ( $\text{Ce}(\text{NO}_3)_6(\text{NH}_4)_2$ , from Fluka), which was contacted with the Pd/H-MOR catalyst for 24 h. Afterwards, the solid was filtered and calcined in air at  $500^\circ\text{C}$  for 2 h.

### 2.2. Catalyst characterization

Metal weight loadings were determined by atomic absorption spectroscopy (AA) and by inductive couple plasma analysis (ICP).

The fresh and used samples of catalysts were also characterized by FTIR spectroscopy of adsorbed species. Infrared spectra were recorded using a NICOLET 20 DXB instrument at  $4\text{ cm}^{-1}$  resolution. Catalyst samples of approximately 30–40 mg were pressed to form transparent disks of 13 mm in diameter that were mounted in a metal holder. The holder was placed in the beam path of a stainless-steel cell, sealed with  $\text{CaF}_2$  windows, and coupled to a vacuum system for evacuation to  $10^{-6}$  Torr. It was possible to perform heat treatments up to  $300^\circ\text{C}$  in air or  $\text{H}_2$  and to dose small amounts of CO and NO. CO and NO adsorption spectra were obtained at room temperature under a gas phase pressure of 5 Torr.

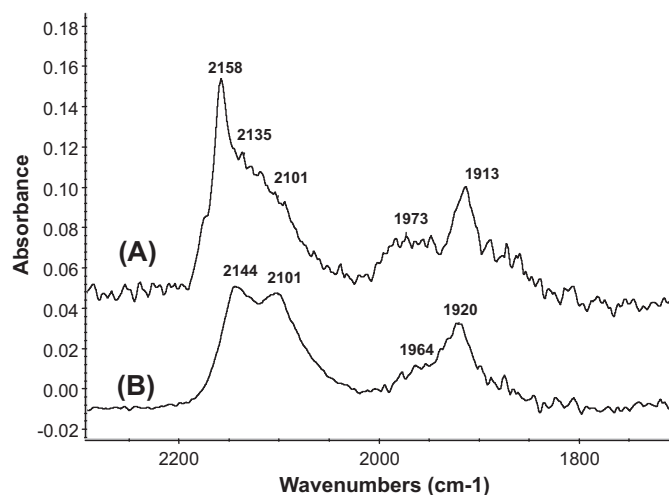


Fig. 1. FTIR spectra of reduced Pd/H-MOR (A) and Ce-Pd/H-MOR (B) catalysts at room temperature after CO exposure to 5 Torr. Samples reduced in situ to  $300^\circ\text{C}$ .

### 2.3. Activity, selectivity and stability of the catalysts

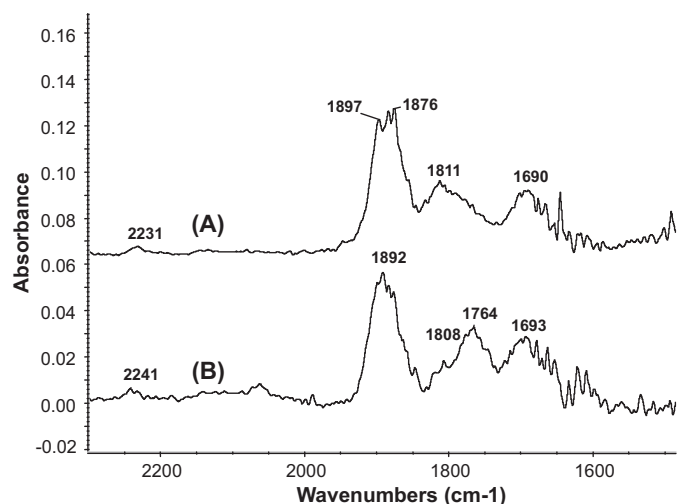
The SCR- $\text{CH}_4$  reaction was carried out in a quartz flow reactor connected to a gas chromatograph, using a  $\text{NO}/\text{CH}_4/\text{O}_2/\text{He}$  gas mixture containing 1010 ppm ( $\pm 1\%$ ) of NO, 3300 ppm ( $\pm 1\%$ ) of  $\text{CH}_4$  and 4.1% of  $\text{O}_2$  in a He balance. This composition was obtained by adjusting the mass flow rate of  $\text{NO}$  (3000 ppm)/He,  $\text{CH}_4$  (4900 ppm)/He and pure  $\text{O}_2$  streams. The catalysts were studied under dry and wet conditions (5%  $\text{H}_2\text{O}$ ).

The reactor effluent was analyzed by on-line gas chromatography using a TCD detector and two Porapak Q columns. One column was held at  $-11^\circ\text{C}$  to separate  $\text{N}_2$ ,  $\text{O}_2$ , NO and  $\text{CH}_4$ , while the other one, which operated at  $80^\circ\text{C}$ , was used to identify  $\text{CH}_4$ ,  $\text{N}_2\text{O}$  and  $\text{CO}_2$ . The quantification of the reaction products was performed from the calculated areas of the chromatographic peaks, corrected with experimental response factors. NO conversion was calculated from the area of the  $\text{N}_2$  and  $\text{N}_2\text{O}$  peaks because NO was partially converted into  $\text{NO}_2$  due to the high oxygen content in the feed mixture. The selectivity to  $\text{N}_2$  was calculated as  $S_{\text{N}_2} (\%) = (\text{ppm de N}_2) / ((\text{ppm de N}_2 + \text{ppm N}_2\text{O}) \times 100$ .

Experiments were carried out at a temperature ranging from  $300^\circ\text{C}$  to  $650^\circ\text{C}$ , using a catalyst mass of 200 mg and a flow rate of  $220\text{ cm}^3/\text{min}$ . (bulk density =  $0.5\text{ g}/\text{cm}^3$ ; S.V.  $\approx 33,000\text{ h}^{-1}$ ). Charges of catalyst in oxidized form were activated in a mixture flow at  $300^\circ\text{C}$  until constant values of conversion were obtained. Next, the temperature was increased in steps of  $50^\circ\text{C}$ , up to  $650^\circ\text{C}$ . Runs were repeated to confirm the results. Water was introduced using a syringe pump. The catalytic activity of each sample was first determined under dry conditions, then in the presence of water, and finally the run was repeated in the absence of water.

## 3. Results and discussion

Fig. 1 depicts the infrared spectra of CO adsorption at room temperature on Pd/H-MOR and Ce-Pd/H-MOR reduced in situ at  $300^\circ\text{C}$ . The monometallic catalyst (Fig. 1(A)) presents a band due to CO adsorbed on  $\text{Pd}^{2+}$  at  $2158\text{ cm}^{-1}$ , overlapping others that extend to frequencies below  $2100\text{ cm}^{-1}$  attributed to the existence of  $\text{Pd}^{x+}$  and  $\text{Pd}^0$ . The oxidizing pretreatment at  $400^\circ\text{C}$  during the preparation step generates  $\text{PdO}$  particles that partly react with protons of the zeolite to form  $\text{Pd}^{2+}$  species by means of the mechanism known as oxidative redispersion [14]. It is important to realize that the concentration of  $\text{Pd}^{2+}$  ions depends on oxidation temperature. At a low oxidation temperature,  $\leq 300^\circ\text{C}$ , the main product is  $\text{PdO}$ . By



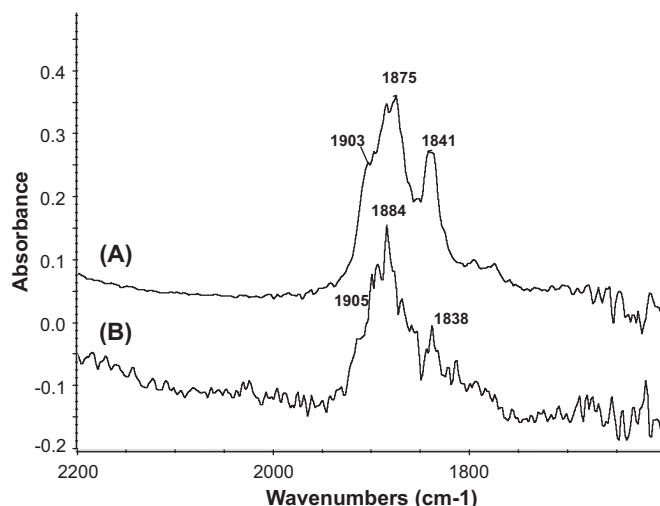
**Fig. 2.** FTIR spectra of reduced Pd/H-MOR (A) and Ce-Pd/H-MOR (B) catalysts at room temperature after NO exposure to 5 Torr. Samples reduced in situ to 300 °C.

increasing the oxidation temperature Pd<sup>2+</sup> ions are produced. These different oxidation products can be identified by TPR experiments. Reifsnnyder et al. [15] observed a single hydrogen consumption peak at 100 °C on a Pd(0.5%)/H-MOR sample calcined at 350 °C that was attributed to the reduction of Pd<sup>2+</sup> to Pd<sup>0</sup>. On the other hand, Homeyer and Sachtler [14] demonstrated that the reduction profile of a 2% Pd/NaY sample calcined at 773 K, exhibited a consumption peak around 473 K. A H<sub>2</sub> consumption peak around 273 K on the sample calcined at ≤300 °C was indicative of PdO presence. Pieterse and Booneveld [13] lately performed a TPR study on a Pd(0.35%)/H-MOR catalyst calcined at 500 °C and found Pd reduction peaks in the 300–450 °C temperature range. After Ce addition the Pd reduction peak was observed at a higher temperature. On our samples the reduction to 300 °C prior to CO adsorption gives place to the formation of a small fraction of metallic Pd characterized by a CO adsorption band at ≈2100 cm<sup>-1</sup>, but most of the metal remains in an oxidized state (Pd<sup>2+</sup>, Pd<sup>+</sup>). The peaks of minor intensity in the 2000–1800 cm<sup>-1</sup> frequency range correspond to multiple coordinated CO adsorption on metallic Pd. This broad band is partially resolved in one peak at 1973 cm<sup>-1</sup> and another one at 1913 cm<sup>-1</sup> attributed to CO adsorbed on the Pd(100) and Pd(111) surface planes, respectively.

Similar bands are observed on the reduced Ce-Pd/H-MOR sample (Fig. 1(B)), although the intensity of the peak due to CO adsorbed on Pd<sup>2+</sup> was attenuated, while the peak intensity due to CO on Pd<sup>0</sup> increased. Bearing in mind that the sample was calcined at 500 °C after Ce incorporation it is impossible to determine whether the changes are due to this pretreatment or to a Ce effect on Pd reduction.

Fig. 2 shows the infrared spectra of NO adsorption at room temperature on reduced samples of Pd/H-MOR (A) and Ce-Pd/H-MOR (B). The broad band at 2231 cm<sup>-1</sup> corresponds to NO<sub>2</sub> adsorption and was identified by Descorme et al. [7]. The band located at 1897 cm<sup>-1</sup> corresponds to NO adsorption on the mordenite. In accordance with other studies, the band at 1876 cm<sup>-1</sup> is assigned to NO adsorption on Pd<sup>2+</sup> [7,8].

Fig. 2(B) also shows a broad, but less intense band with a maximum at 1811 cm<sup>-1</sup>. This one might correspond to NO adsorption on Pd<sup>x+</sup> species. Due to NO adsorption on Pd<sup>0</sup>, a small band at 1740 cm<sup>-1</sup> was expected. However, this band may be overlapped by the one located at 1693 cm<sup>-1</sup>, which was not identified. On Ce-Pd/H-MOR the spectrum shows a similar band due to NO on the support and NO adsorbed on Pd<sup>2+</sup> at ≈1892 cm<sup>-1</sup>. A new band appears at 1764 cm<sup>-1</sup> reflecting a higher concentration of Pd<sup>0</sup>

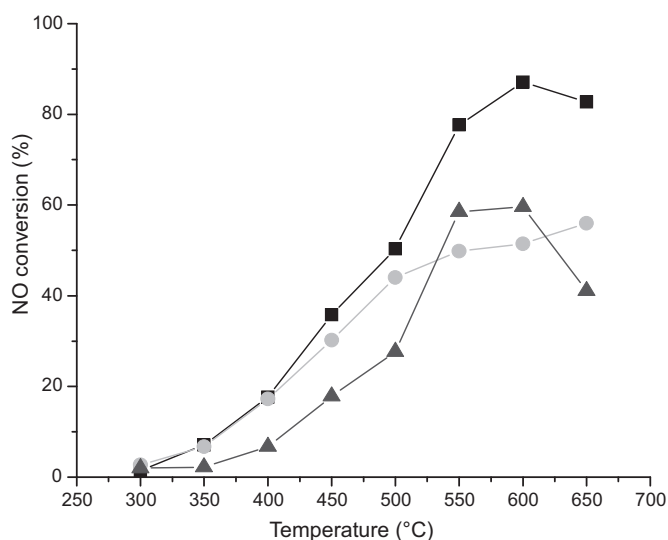


**Fig. 3.** FTIR spectra of oxidized Pd/H-MOR (A) and Ce-Pd/H-MOR (B) catalysts at room temperature after NO exposure to 5 Torr. Samples oxidized in situ to 300 °C.

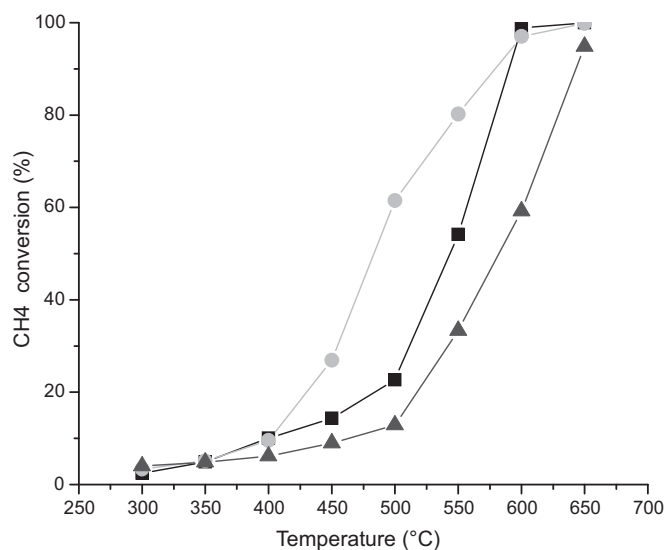
sites, as observed on the CO adsorption spectrum after Ce addition.

The catalysts were also characterized by NO adsorption after a treatment in air at 300 °C, a condition that resembles the surface state prior to reaction. The Pd/H-MOR spectrum in Fig. 3(A) exhibits a main band at 1875 cm<sup>-1</sup> due to NO on Pd<sup>2+</sup> and another one at 1841 cm<sup>-1</sup> that Descorme et al. [7] assigned to dinitrosyl species (Pd(NO)<sub>2</sub>). On Ce-Pd/H-MOR this band was not observed clearly.

The NO conversion as a function of temperature for the Pd/H-MOR catalyst is shown in Fig. 4 under different reaction conditions. A maximum conversion of 90% was obtained at 600 °C in the absence of water. This behavior was clearly altered in the presence of water; the conversion increased continuously, but the highest value was ≈60% at 650 °C. When water was removed from the feed mixture, the initial activity (dry condition on fresh sample) was not recovered, but 60% conversion was obtained at 550–600 °C. The effect of water on CH<sub>4</sub> conversion was similar, as shown in Fig. 5: it decreased markedly in the whole temperature range. However, after reverting to the dry condition, the activity for CH<sub>4</sub> combustion was higher than the initial value, thus suggesting a modification of the catalyst surface. This behavior accords with an increase in the



**Fig. 4.** NO conversion vs. temperature on Pd/H-MOR. (■) Dry feed; (▲) wet feed; (●) dry feed on sample exposed to water.

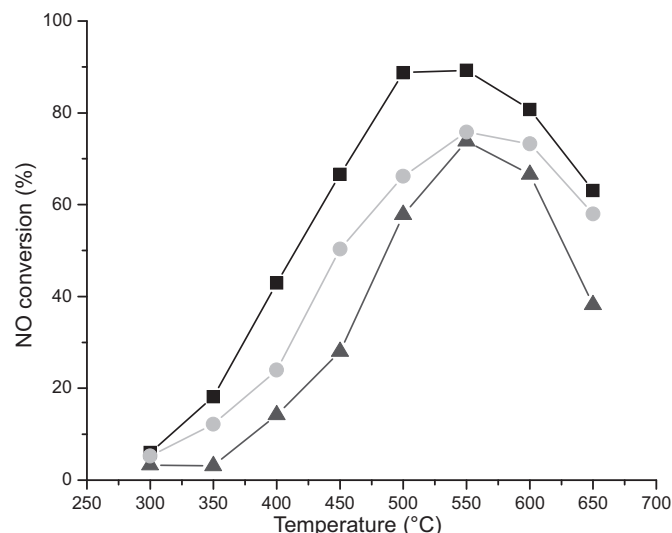


**Fig. 5.** CH<sub>4</sub> conversion vs. temperature on Pd/H-MOR. (■) Dry feed; (▲) wet feed; (●) dry feed on sample exposed to water.

fraction of Pd present in an oxidized form (PdO). The FTIR spectra of adsorbed CO on the fresh and used samples are compared in Fig. 6. It is observed that the band due to CO on Pd<sup>2+</sup> at 2158 cm<sup>-1</sup> was attenuated, while the band due to CO adsorbed on the linear and bridge form on Pd<sup>0</sup> became more intense on the used sample. The decrease in the concentration of Pd<sup>2+</sup> species explained the lower conversion of NO, while the presence of a larger amount of Pd in metallic form justifies the increased conversion of CH<sub>4</sub>.

These results are in accordance with those reported by Ohtsuka and Tabata [9] mentioned in the Introduction section. By using Raman spectroscopy they demonstrated that H<sub>2</sub>O facilitates the Pd agglomeration that leads to the formation of PdO crystals that favor CH<sub>4</sub> combustion.

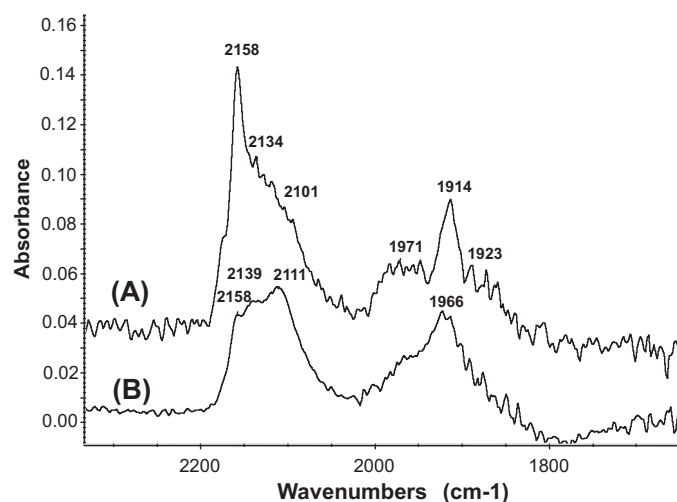
When the Ce–Pd/H-MOR catalyst was tested under dry and wet conditions, important differences in the activity were observed (Fig. 7). For NO reduction the activity was higher than Pd/H-MOR's in the investigated temperature range. It reached a value of 90% at 500–550 °C, that is at a lower temperature. In addition, NO conversion was less affected by water presence: it decreased to 75% at 550 °C. Upon returning to dry conditions, the initial activity of the



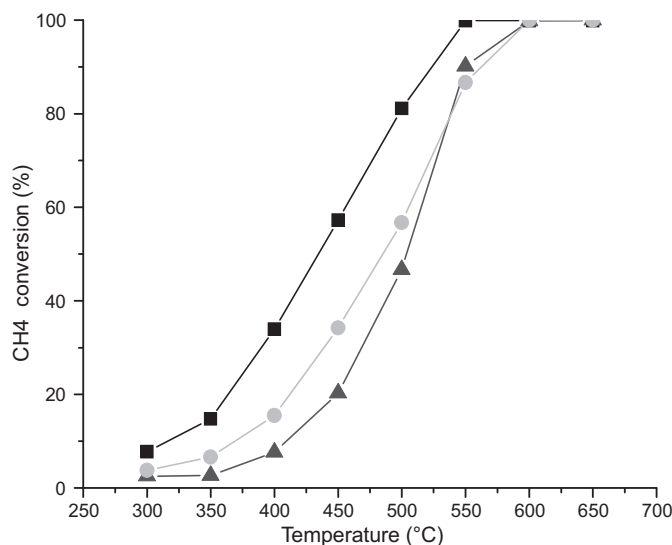
**Fig. 7.** NO conversion vs. temperature on Ce–Pd/H-MOR catalyst. (■) Dry feed; (▲) wet feed; (●) dry feed on sample exposed to water.

Ce-modified catalyst was partially recovered, thus indicating that some alteration of the catalyst surface had occurred. The Ce effect on CH<sub>4</sub> conversion is shown in Fig. 8. Under dry and wet conditions the activity is higher than Pd/H-MOR's (see Figs. 5 and 8). In water presence the activity decreases, mainly in the low temperature range. Upon reverting to dry conditions, the initial activity is partially recovered, a behavior that is quite different from the one observed on Pd/H-MOR.

In order to observe the alterations produced on the catalyst surface during the conversion vs. temperature runs, the FTIR spectrum of adsorbed CO on a used sample was compared with one of a fresh sample. The results are shown in Fig. 9. In this case the spectra are quite similar; the band due to CO adsorbed on Pd<sup>2+</sup> species decreased slightly and those corresponding to CO on metallic Pd exhibited small changes at 2100 and 1920 cm<sup>-1</sup>. Consequently, it is clear that Ce addition has a beneficial effect on the activity and also on the stability of the Pd/H-MOR catalyst for SCR-CH<sub>4</sub>. According to the FTIR results, Ce stabilizes the active Pd species (Pd<sup>2+</sup>). If the promoter is located in exchange positions as Ce<sup>3+</sup>, it may inhibit the dealumination process in water presence, enhancing the ther-



**Fig. 6.** FTIR spectra of reduced Pd/H-MOR catalysts at room temperature after CO exposure to 5 Torr. (A) Fresh sample, (B) used sample. Samples reduced in situ to 300 °C.



**Fig. 8.** CH<sub>4</sub> conversion vs. temperature on Ce–Pd/H-MOR catalyst. (■) Dry feed; (▲) wet feed; (●) dry feed on sample exposed to water.



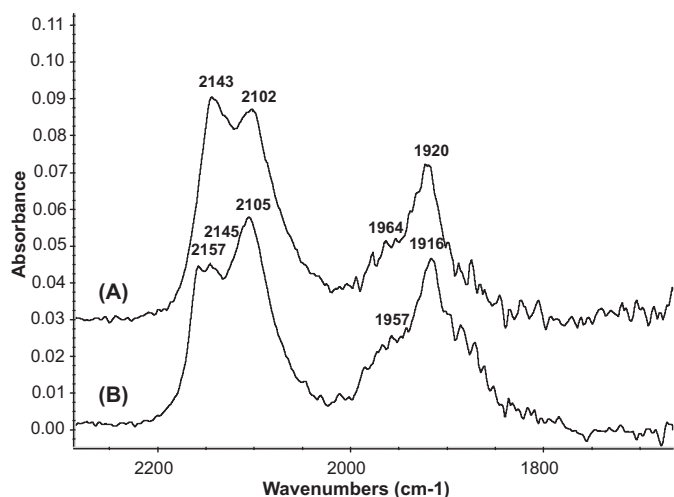


Fig. 9. FTIR spectra of reduced Ce-Pd/H-MOR at room temperature after CO exposure to 5 Torr. (A) Fresh sample, (B) used sample. Samples reduced in situ to 300 °C.

mal stability of the zeolite and preventing PdO formation. However, the presence of small CeO<sub>2</sub> particles cannot be discarded taking into account the method used for Ce addition. According to our results, Ce enhances CH<sub>4</sub> combustion and this behavior suggests the presence of cerium oxide, probably in the outer surface of the zeolite. We have verified that the BET surface area and the pore size distribution of Pd/H-MOR were not modified by the addition of cerium. It was reported [16] that Ce<sup>3+</sup> does not promote CH<sub>4</sub> combustion. Taking into account that the presence of Ce also modifies the reducibility of Pd [13], we cannot discard an influence of Ce on the redox reaction. In addition, water adsorption on cerium oxide may reduce its effect on the catalytic reaction. It has also been reported [13] that Ce catalyzes the oxidation of NO to NO<sub>2</sub>, which in turn may increase the activity for NO<sub>x</sub> reduction.

According to the previous discussion, several explanations could be offered about the beneficial role of Ce on Pd/H-MOR catalysts for the SCR-CH<sub>4</sub> reaction. As mentioned by the reviewers, a better characterization of the CeO<sub>x</sub> phase is necessary in order to determine the main role of cerium.

We have also investigated the effect of water and Ce on reaction selectivity focusing the attention mainly on the formation of N<sub>2</sub> and N<sub>2</sub>O. As shown in Fig. 10, a significant N<sub>2</sub>O amount is formed in the 300–400 °C, mainly under dry conditions. N<sub>2</sub>O is nearly absent above 450 °C. Under dry condition, Ce addition increases N<sub>2</sub> selectivity from less than 20% to >60% at 300 °C. There is a remarkable effect of water on N<sub>2</sub> selectivity, which is higher than 90% for Pd/H-MOR and Ce-Pd/H-MOR for a wet feed. When water was eliminated, the catalysts exhibited a decrease in selectivity, but this effect was less pronounced for Ce-Pd/H-MOR.

Experiments were also performed at constant temperature (550 °C) in the presence of water in order to test the stability of the catalysts at a high conversion level. On Pd/H-MOR the conversion decreased from 61 to 57% in 3 h. On the other hand, Ce-Pd/H-MOR activity was constant with 70% conversion after 3 h. We recognize the need to perform longer runs for a more conclusive demonstration of the beneficial effect of Ce on the SCR-CH<sub>4</sub> reaction under wet conditions.

The preceding results demonstrate that Ce promotes the activity, the selectivity and the stability of Pd supported on mordenite for NO elimination with CH<sub>4</sub> in the presence of oxygen and water, in agreement with Pieterse et al.'s previous study [11]. However, our activity results cannot be compared due to differences in catalyst's and reaction conditions. In the mentioned study the Pd content and the CH<sub>4</sub>/NO ratio were higher, 0.4% and 5 respectively, and the

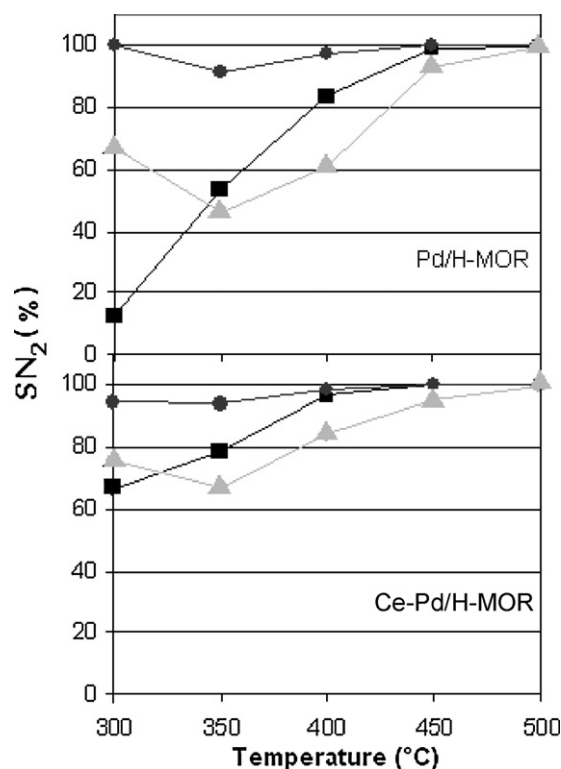


Fig. 10. Selectivity to N<sub>2</sub> as a function of temperature on Pd/H-MOR and Ce-Pd/H-MOR catalysts. (■) Dry feed; (●) wet feed; (▲) dry feed after exposure to water.

space velocity was lower (S.V. = 17,000 h<sup>-1</sup>). By using similar water, oxygen and Ce concentrations, they obtained an NO conversion of 60% at 375 °C, while the CH<sub>4</sub> conversion was much lower (20%). Under these conditions practically no deactivation was observed after a test run of 100 h.

It is appropriate to compare our results with Bustamante et al.'s [17], who studied the SCR-CH<sub>4</sub> reaction on a Pd(0.15%)/Co(4.8%)H-MOR catalyst. By using a similar NO and CH<sub>4</sub> concentration, but a higher content of oxygen (6%) and water (8%) in the feed mixture, they obtained conversions of 90% and 60% at 550 °C, respectively. These results are in agreement with those presented here. However, Pieterse et al. [11,18] demonstrated that the deactivation behavior of the Co promoted catalyst is similar to Pd/H-MOR's. This disadvantage may perhaps be overcome by Ce addition.

#### 4. Conclusions

The FTIR characterization of a Pd/H-MOR catalyst confirms the presence of Pd<sup>2+</sup> species, which are responsible for the high catalytic activity for the selective reduction of NO with CH<sub>4</sub> in oxygen presence. Under dry conditions NO conversion was 90% at 600 °C. The presence of water has a negative effect on NO and CH<sub>4</sub> conversion. The concentration of active Pd<sup>2+</sup> species decreases and Pd particles that favor CH<sub>4</sub> combustion under dry conditions are formed. This change in surface structure cannot be reversed if water is removed from the feed. Ce addition to Pd/H-MOR catalyst improves the activity for NO conversion and the selectivity to N<sub>2</sub>. In the presence of water, NO conversion was 76% with 100% selectivity to N<sub>2</sub> at 550 °C. The presence of Ce also enhanced CH<sub>4</sub> combustion under wet conditions. The FTIR spectrum of adsorbed CO has shown that Ce inhibits the transformation of active Pd<sup>2+</sup> species into PdO under reaction conditions.

## References

- [1] M.J. Iwamoto, J. Weitkamp, H.G. Karge, H. Pfeifer, H. Holderich (Eds.), *Zeolites and Related Microporous Materials*, vol. 84, 1994, p. 1395.
- [2] Y. Nishizaka, M. Misono, *Chem. Lett.* (1993) 1295.
- [3] Y. Nishizaka, M. Misono, *Chem. Lett.* (1994) 2237.
- [4] C.J. Loughran, D.E. Resasco, *Appl. Catal. B* 7 (1995) 113.
- [5] A. Ali, W. Alvarez, C.J. Loughran, D.E. Resasco, *Appl. Catal. B* 14 (1997) 13.
- [6] Y. Chin, A. Pisanu, L. Serventi, W. Alvarez, D. Resasco, *Catal. Today* 54 (1999) 419.
- [7] C. Descorme, P. Gelin, C. Lécuyer, M. Primet, *J. Catal.* 177 (1998) 352.
- [8] K. Shimizu, F. Okada, Y. Nakamura, A. Satsuma, T. Hattori, *J. Catal.* 195 (2000) 151.
- [9] H. Ohtsuka, T. Tabata, *Appl. Catal. B* 21 (1999) 133.
- [10] L.F. Córdoba, M. Flytzani-Stephanopoulos, C. Montes de Correa, *Appl. Catal. B: Environ.* 33 (2001) 25.
- [11] J.A.Z. Pieterse, R.W. van den Brink, S. Booneveld, F.A. de Bruijn, *Studies in Surface Science and Catalysis*, vol. 154, Elsevier, 2004, p. 2522.
- [12] J.A.Z. Pieterse, H. Top, F. Vollink, K. Hoving, R.W. van den Brink, *Chem. Eng. J.* 120 (2006) 17.
- [13] J.A.Z. Pieterse, S. Booneveld, *Appl. Catal. B: Environ.* 73 (2007) 327.
- [14] S.T. Homeyer, W.M.H. Sachtler, *Appl. Catal. A: 54* (1989) 189.
- [15] S.N. Reifsnnyder, M.M. Otten, H.H. Lamb, *Catal. Today* 39 (1998) 317.
- [16] Z. Li, M. Flytzani-Stephanopoulos, *Appl. Catal. A* 165 (1997) 15.
- [17] J.A.Z. Pieterse, R.W. van den Brink, S. Booneveld, F.A. de Bruijn, *Appl. Catal. B: Environ.* 46 (2003) 239.
- [18] F. Bustamante, F. Córdoba, M. Yates, C. Montes de Correa, *Appl. Catal. A* 234 (2002) 127.