Redispersion of Pd on acidic supports and loss of methane combustion activity during the selective reduction of NO by CH_4

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The CH_4 combustion, occurring under selective NO reduction conditions, has been investigated over several Pd catalysts. In the presence of NO and support acidity, the combustion activity of Pd is drastically inhibited. Highly dispersed Pd/acidic zeolites compare favorably with other SCR catalysts. At 500 °C, a 0.3% Pd/H-ZSM-5 sample exhibited a better performance than a typical Co-ZSM-5 catalyst.

Keywords: stabilization, Pd^{2+} ions, EXAFS, SCR, NO_x, acidic supports, H-ZSM-5, H-mordenite, sulfated zirconia

1. Introduction

Using methane as a reductant for the abatement of NO from stationary sources [1,2] would have obvious advantages over other reductants such as ammonia and higher hydrocarbons. However, one of the main difficulties initially encountered when methane was used as a reductant in lean mixtures was its poor selectivity towards the reaction with NO as opposed to O_2 [3,4]. Nonetheless, in recent years, some catalysts have been found to be highly selective, even in the presence of excess oxygen. Among them, zeolites such as ZSM-5 or ferrierite, containing Co, Ni, Mn, In, or Ga appear as the most promising candidates [5–10]. Palladium has received much less attention due to its very high activity as a total combustion catalyst. In fact, Pd is a very active catalyst for the $NO + CH_4$ reaction in the absence of excess O_2 [11], but in the presence of excess O_2 the selectivity strongly depends on the type of support used. For example, when Pd is supported over SiO_2, or other inert supports, the oxidation of methane occurs at high rates, leaving NO unconverted. A markedly different behavior was obtained when the support contained acidity [12]. Misono et al. [13–15] were the first to observe that, while Pd/Na-ZSM-5 was totally unselective, Pd/H-ZSM-5 showed very high selectivity in the presence of 2% O_2. We have similarly found that, not only H-ZSM-5, but also H-mordenite [12] and non-zeolitic acidic supports such as SO_4/ZrO_2 and, to a lesser extent, SiO_2–Al_2O_3, were able to promote the selectivity enhancement [12].

In a recent X-ray absorption study [16] conducted on several Pd catalysts, we have found that, upon exposure to the reaction mixture ($CH_4 + NO + O_2$), the morphology of the oxidized Pd species strongly depends on the metal loading and the acidity of the support. On low Pd-loading catalysts over acidic supports, the metallic Pd-particles, initially present on the catalyst, are rapidly transformed into Pd^{2+} ions by the reaction mixture. By contrast, on the non-acidic materials, the Pd particles are transformed into PdO clusters. We have ascribed the high selectivity exhibited by low-loading Pd catalysts supported on acidic materials to the stabilization of those Pd^{2+} ions. However, direct involvement of the acid sites in the reaction cannot be ruled out.

It is understood here that, although Pd^{2+} are the most common ionic species that can be stabilized in the zeolite, stabilization of other Pd^{n+} species could also occur. Therefore, we will use the term Pd^{n+} to indicate ionic species stabilized by the support that are not forming PdO clusters. Supporting evidence for the stabilization of Pd^{n+} ions on H-ZSM-5 in the presence of NO_x has been independently found in recent TPR studies by Adelman and Sachtler [17] as well as in FTIR studies by Bell et al. [18]. Although the exact mechanism of Pd^{n+} stabilization is still unclear, it most probably involves the Brønsted sites of the zeolite in the way previously described for the case of Pd/H-Y zeolites [19]. The FTIR investigation [18] demonstrated that although under O_2, the H-ZSM-5 zeolite can stabilize a small amount of Pd, the redispersion under NO is much more effective and a larger amount of Pd can be stabilized.

It has been proposed [14,15] that the combustion activities in the absence of NO and the overall methane conversion (from the direct oxidation and SCR reaction) in the presence of NO are the same on H-ZSM-5 and Na-ZSM-5, despite the great differences exhibited in the NO reduction and methane combustion rate under SCR conditions. As illustrated in the present contribution, we believe that measuring the combustion activity in the absence of NO does not reflect the actual combustion activity during the SCR reaction. In the presence of NO and Brønsted sites, the combustion activity of Pd is drastically inhibited and this

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inhibition is, at least, partially responsible for the observed enhancements in selectivity.

2. Experimental

Various Pd catalysts supported on acidic and non-acidic supports were investigated. The Na-ZSM-5 (Zeocat Pentasil PZ-2/54 Na, $SiO_2/Al_2O_3 = 24.3$) was obtained from Chemie Uetikon and converted to the protonic form (H-ZSM-5) by ion exchange with a 2.25 M NH_4Cl solution in a ratio of 20 cm^3/g zeolite. The ion exchange was carried out by boiling the exchange solution in reflux for 2 h. After the exchange, the slurry was centrifuged to separate the zeolite, which was washed with ultra-pure water. The same exchange procedure was repeated three times. Following the final exchange and washing, the zeolite was dried overnight at 110 °C. Lastly, to convert the NH_4-ZSM-5 to the final H-ZSM-5, a thin cake of the zeolite was heated up to 550 °C for 30 min and then treated at 550 °C for 2 h in flowing nitrogen. Silica (T1571, BET surface area = 130 m^2/g) was obtained from United Catalysts and used as received. The H-mordenite (LZ-M-8, SiO_2/Al_2O_3 ratio = 8) was received from UOP and used as received. Varying Pd loadings were accomplished by the incipient wetness impregnation method using aqueous solutions of a Pd salt ($Pd(NO_3)_2 \cdot H_2O$, 39.95% Pd, Johnson Mathey). The liquid/solid ratio to obtain incipient wetness was determined for each support and it ranged from 0.6 to 0.9 cm^3/g.

The catalytic activity measurements were conducted in a quartz tube reactor. Prior to each experimental run, the catalysts were pretreated *in situ* by heating in H_2 or pure He from room temperature to 500 °C at a heating rate of 5 °C/min. The products and reactants were analyzed by gas chromatography and GC-MS, using the capillary columns Molsieve 5A and Porabond Q PLOT, respectively. The results of most runs are reported as conversion of NO to N_2, based on N_2 production. For some selected runs, the conversion, based on NO consumption, was determined. Both results were essentially the same. The only by-product detected by GC-MS in very small quantities was N_2O. The NO conversion to N_2O was lower than 0.8%.

EXAFS spectra were obtained at the National Synchrotron Light Source (NSLS) in Brookhaven National Laboratory, Upton, New York using beamline X-18b. The EXAFS data were obtained in transmission mode near the K-edge of Pd (24 350 eV), using a sample cell that allowed gases to flow over the sample and cool it to liquid-nitrogen temperature. The beamline used a Si(111) crystal monochromator to vary the photon energy incident to the sample. The EXAFS data were analyzed using both experimental and theoretical reference standards. EXAFS spectra were taken of Pd foil at room temperature and PdO powder at liquid-nitrogen temperature and were used as standards for the Pd–Pd and Pd–O interactions. Theoretical standards were generated by the program FEFF [20,21] for metallic Pd and PdO particles. Details of the data analysis procedure have been presented elsewhere [16].

3. Results and discussion

In previous work [12], we showed that the NO conversion obtained over a series of Pd/H-ZSM-5 catalysts was a strong function of the Pd loading. It was observed that the NO conversion initially increased with the amount of Pd impregnated in the zeolite, reached a maximum at about 0.3 wt% Pd, and then decreased. Figure 1 illustrates this trend and compares that behavior with a similar one exhibited by the Pd/H-Mor series. These activity measurements were obtained at a GHSV of 10 000 h^{-1} after 60 min on stream, at 500 °C, and using the following feed composition: 4800 ppm NO, 9700 ppm CH_4, and 2.5% O_2, with the balance He.

It is observed that in the Pd/H-Mor series the maximum occurred at a somewhat lower Pd loading than in the Pd/H-ZSM-5 series, but the overall trend was the same. It is important to note that, in both series, the drop in NO conversion at high Pd loadings was not accompanied by a drop in CH_4 conversion, indicating that the CH_4 combustion (direct oxidation by O_2) strongly increased with Pd loading. In a recent XANES/EXAFS investigation of these catalysts we showed that, on low-loadings Pd/H-ZSM-5 catalysts, Pd^{2+} ions were present after the SCR reaction [16]. By contrast, on the higher loading Pd/H-ZSM-5 catalysts, PdO clusters appeared after reaction. Therefore, it can be concluded that the higher combustion activity of the high-loading Pd catalysts can be ascribed to the presence of these PdO clusters.

We have compared the intrinsic combustion activity of Pd on various supports at different loadings. This comparison is illustrated in figure 2, which shows the light-off curves for three samples. A clear trend was observed, the

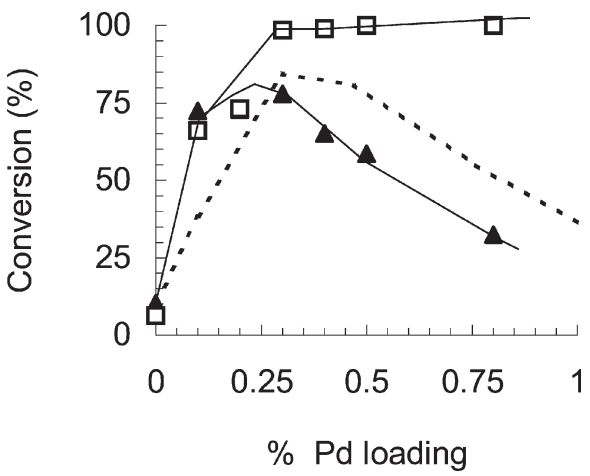

Figure 1. Effect of Pd loading on SCR reaction. NO (▲) and CH_4 (□) conversions at 500 °C, after 60 min on stream, as a function of Pd loading over Pd/H-mordenite catalysts. The NO conversion trend (dashed line) obtained under the same conditions over the Pd/H-ZSM-5 series is included for comparison.

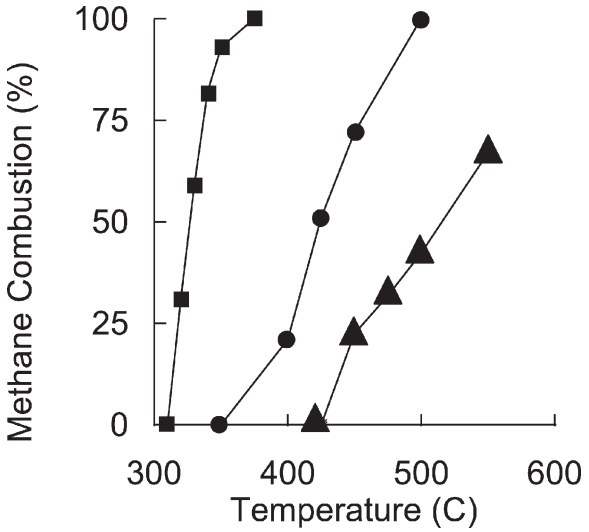

Figure 2. Methane combustion as a function of temperature over various Pd catalysts. 0.3% Pd/silica (■), 0.3% Pd/H-Mor (●), and 0.1% Pd/H-Mor (▲). GHSV 10 000 h^{-1}. Feed conditions: 9700 ppm CH_4, 2.5% O_2 with the balance He.

light-off temperature noticeably increased in the sequence 0.3% Pd/SiO_2 < 0.3% Pd/H-Mor < 0.1% Pd/H-Mor. This trend, which was also observed with the Pd/H-ZSM-5 series is in agreement with the concepts proposed above. That is, the combustion activity was markedly reduced on the zeolite-supported low-loading catalysts, where Pd was highly dispersed and in close interaction with the support, most probably in the form of isolated ions, stabilized by Brønsted sites inside the zeolite [18]. That situation is certainly most favorable in the 0.1% Pd/H-Mor, less favorable in the 0.3% Pd/H-Mor, and not possible on the silica-supported catalyst. In the latter case, we have confirmed by EXAFS analysis that, following the CH_4 combustion reaction, Pd was in the form of PdO clusters [16]. It is certainly possible that these PdO clusters undergo oxidation and surface reconstruction to yield a more active phase for direct methane oxidation, as has been independently proposed by Hicks et al. [22,23], and Baldwin and Burch [24] on alumina-supported catalysts. In a recent study by Fujimoto et al. [25], the higher methane combustion activity of large PdO_x crystallites was ascribed to weaker Pd–O bonds, which participate in a redox reaction. In comparison to PdO clusters, isolated Pd ions in highly dispersed catalysts where metal–support interactions are strong are expected to have stronger Pd–O bonds and, consequently to be less active for methane combustion.

It is then expected that during the SCR reaction, that is, in the presence of NO, low-loading Pd catalyst supported on acidic materials would mostly be in highly dispersed state. Therefore, we expect a lower combustion activity in the presence than in the absence of NO. Then, it is essential to estimate the combustion activity of the different catalysts *under* SCR conditions. In order to compute the fraction of CH_4 that is consumed in the direct oxidation by O_2 as

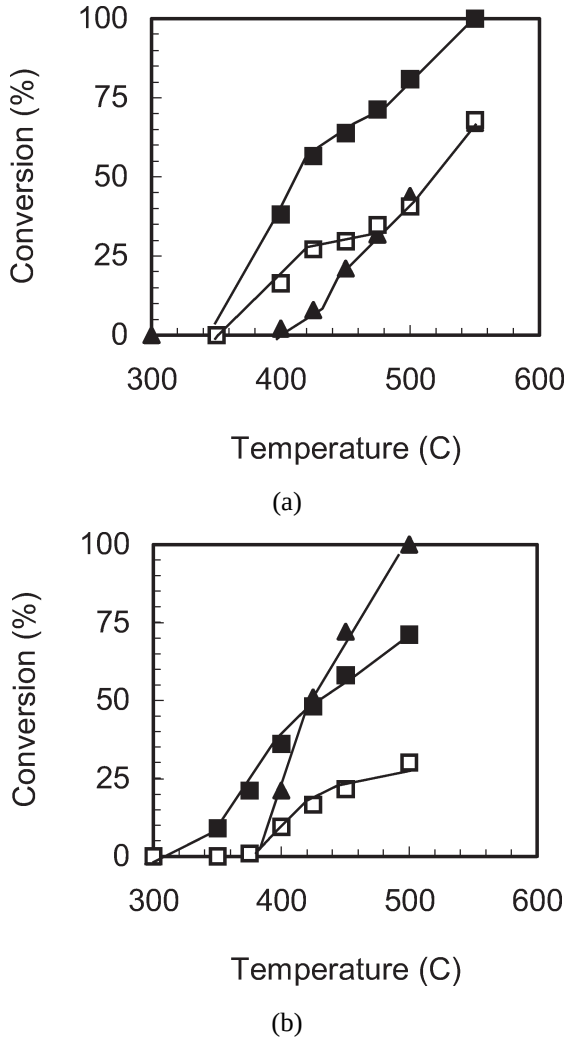

Figure 3. Methane conversion as a function of reaction temperature with and without NO present in the feed. (▲) CH_4 conversion under $CH_4 + O_2$ reaction; (■) CH_4 conversion under $CH_4 + O_2 + NO$ reaction; (□) CH_4 combustion under $CH_4 + O_2 + NO$ reaction. (a) 0.1 wt% Pd/H-Mor catalyst; (b) 0.3 wt% Pd/H-Mor catalyst.

opposed to the reduction of NO, we have considered the following stoichiometric equations:

$$CH_4 + 2NO + O_2 \rightarrow CO_2 + 2H_2O + N_2 \quad (1)$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad (2)$$

By taking into account the CH_4/NO feed ratio and measuring the overall CH_4 and NO conversion, it is straightforward to calculate the fraction of methane converted through reaction (2) (methane combustion).

Figure 3 (a) and (b) compares the methane conversions obtained in the presence and absence of NO in the feed over Pd/H-Mor catalysts with 0.1 and 0.3 wt% loading. The data for CH_4 combustion by O_2, in the absence of NO, were taken from figure 2. In this case, the 0.3% Pd sample shows a higher combustion activity than the 0.1% Pd sample. A remarkable contrast is observed in the presence of NO. While on the 0.1% Pd, a much higher overall CH_4 conversion was obtained with than without NO, on

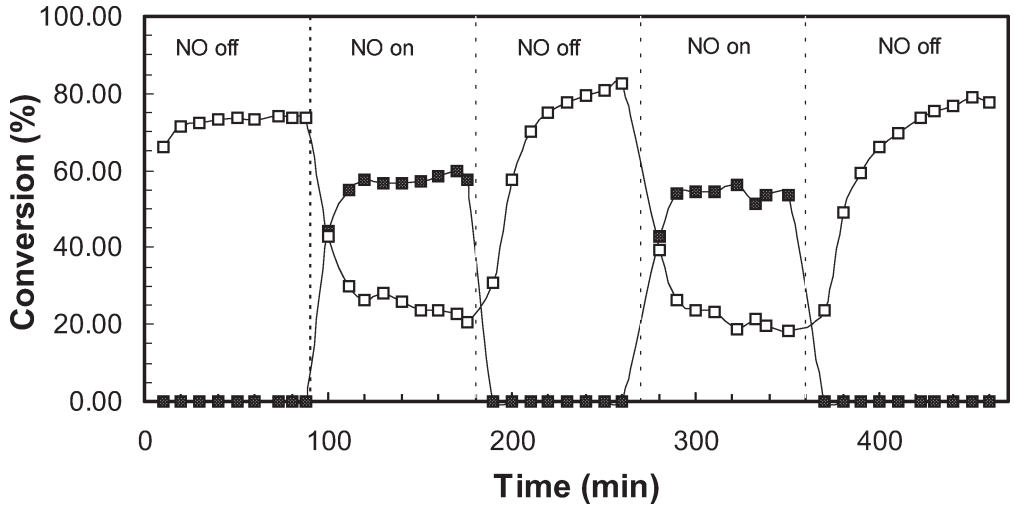

Figure 4. Methane combustion and NO conversion as a function of time on stream over 0.3 wt% Pd/H-ZSM-5 while turning NO on and off. Feed conditions: [NO] = 3 560 ppm, [CH_4] = 7 440 ppm, [O_2] = 1.87%; GHSV = 6 900 h^{-1}; T = 500 °C. (□) Methane combustion, (■) NO conversion.

the 0.3% Pd, the increase was only apparent at lower temperatures. In fact, at high temperatures, the overall CH_4 conversion was lower in the presence of NO than without NO. As a result, the computed combustion of CH_4 in the presence of NO, greatly decreases on the 0.3% Pd catalyst as compared to the $CH_4 + O_2$ alone, while it does not decrease on the 0.1% Pd catalyst. These changes, occurring in the presence of NO, make the combustion under SCR conditions about the same for both catalysts, even though in the absence of NO their combustion activities were very different. These results can be explained in terms of the ability of NO to help in the stabilization of Pd^{n+} ions. In the 0.1% Pd/H-Mor catalyst, most of the Pd may be in the form of isolated Pd^{n+} ions and, as a result, its combustion activity is low whether NO is present in the feed or not. By contrast, on the 0.3% Pd/H-Mor in the absence of NO, there may be a relatively large amount of PdO clusters, which are very active for CH_4 combustion, but when NO is present, they are converted into Pd^{n+} ions. As mentioned above these ions have a lower combustion activity.

In order to observe the transition in combustion activity in the absence and in the presence of NO, we have conducted measurements of methane conversion as a function of time over the same 0.3 wt% Pd/H-ZSM-5 sample while turning the NO flow on and off. The CH_4 and O_2 concentrations were kept constant at 7 440 ppm and 1.87%, respectively, while the NO concentration was 3 560 ppm or zero. As shown in figure 4, at a 6 900 GHSV the catalyst had a high combustion activity in the absence of NO, but when the NO flow was turned on, the combustion activity drastically dropped to ca. 20%, as the NO conversion increased to 60% in 20 min. The catalyst regained its combustion activity as the NO flow was interrupted and it dropped again when NO was reintroduced. This cyclic behavior indicates that the transformation associated with the presence of NO is reversible.

In a previous work [12], we prepared a series of physical mixtures of Pd/SiO_2 and acidic supports to determine

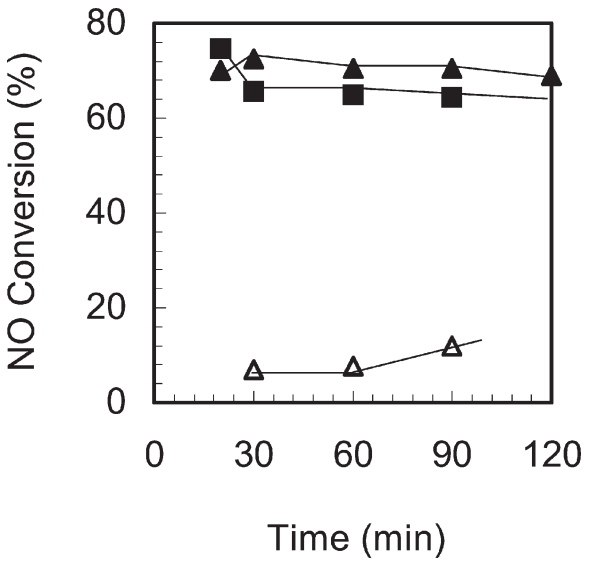

Figure 5. NO conversions obtained in the NO + CH_4 + O_2 (SCR) reaction over the following physical mixtures: (△) 1% Pd/H-ZSM-5 + H-ZSM-5 (no pretreatment); (▲) 1% Pd/H-ZSM-5+H-ZSM-5 (exposed to NO at 500 °C, 20 h); (■) 0.3% Pd/SiO_2 + H-ZSM-5 (exposed to NO at 500 °C, 20 h).

whether the observed promotion by acidic supports were due to a direct interaction between the support and Pd, or was just the addition of two separate functions that resulted in a higher selectivity. The experimental result was that the physical mixtures, particularly those that included sulfated zirconia as the acid component, showed an increased NO conversion compared to the two independent components (i.e., Pd and acidic material). At that time, we concluded that either the reaction was bifunctional and each component participated in the reaction, or a migration of Pd species from one particle to another was taking place. In this contribution, we will further consider this possibility.

Figure 5 shows the NO conversion obtained on three different physical mixtures. The first was a 1 : 2 mixture of 1% Pd/H-ZSM-5 and H-ZSM-5 without previous treatment.

The mixture was heated in He to 500 °C and then exposed to the SCR reaction mixture. It has been previously shown that the 1% Pd/H-ZSM-5 catalyst alone is totally unselective resulting in 100% conversion of CH_4 while the NO conversion is practically zero. With the physical mixture, the NO conversion was less than 10%, but slightly raised with time-on-stream. A remarkable increase in activity was obtained with the second sample for which the physical mixture was heated in NO at 500 °C for 20 h before reaction. In this case, under the same conditions as those used in the previous run, the NO conversion jumped to 70%. A similar NO conversion level was obtained with the third sample, which was a 1 : 2 mixture of 0.3% Pd/SiO_2 and H-ZSM-5 pretreated in NO at 500 °C for 20 h. Similar to the 1% Pd/H-ZSM-5, the 0.3% Pd/SiO_2 catalyst alone was totally unselective.

To rationalize the dramatic changes in selectivity observed after long exposures to NO, we have conducted EXAFS analysis on the physical mixtures of 1% Pd/H-ZSM-5 + H-ZSM-5, after 15 min under SCR conditions and after exposure to NO 20 h at 500 °C. As shown in figure 6, the changes in the FT spectra are remarkable and, as described below, they clearly demonstrate that PdO clusters dominate in the former, while isolated Pd^{n+} ions are the main species in the latter.

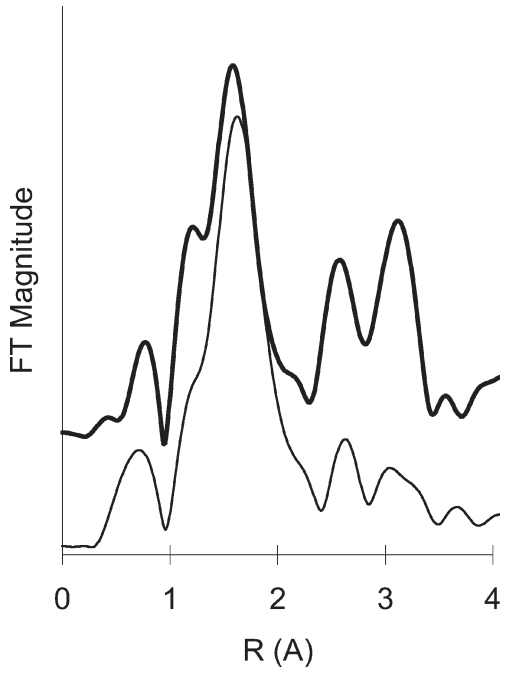

Figure 6. Fourier transform of the EXAFS data obtained on a physical mixture of 1% Pd/H-ZSM-5 and H-ZSM-5 at liquid nitrogen temperature after the following pretreatments: upper curve – reaction in $NO+CH_4+O_2$ (SCR) at 500 °C for 15 min; lower curve – exposed to NO at 500 °C, 20 h.

As described elsewhere [16], a theoretical model of tetragonal PdO can be used to analyze the data of the used Pd catalysts. In this crystal structure, the Pd atom is surrounded by four O atoms located at a distance $R_1 = 2.0194$ Å from the central Pd. The second shell is composed of four Pd atoms at $R_2 = 3.036$ Å, and the third shell is composed of eight Pd atoms at $R_3 = 3.4209$ Å. These bond distances correspond to the uncorrected peaks that appear in the FT data at about 1.6, 2.6, and 3.0 Å, respectively. This model was used to fit the data of the two samples. The fitting of the data in the r-space was done over the range 0.6–4.0 Å, which includes three shells. The $k^1\chi$ data were taken from the k space range of 2.5–12.5 $Å^{-1}$. The relative coordination number (N/N_0) and half path length (R) were varied for each of the shells. The Debye–Waller factor was varied for only the first shell and set to a typical value of 0.003 for the other shells. The results of the fitting routine are summarized in table 1. They clearly show that the sample exposed to NO for a long time exhibits a much lower number of second and third coordination shells, indicating that, on this sample, the number of PdO aggregates have been severely reduced and most of the Pd is forming isolated Pd^{n+} ions.

A clear trend now emerges. When the Pd loading is very low (e.g., 0.1%) the redispersion and stabilization of Pd^{n+} ions readily occurs in oxidizing atmospheres, even in the absence of NO, and the combustion rate is low. At intermediate Pd loadings (e.g., 0.3%) total stabilization of Pd^{n+} ions only occurs in the presence of NO. Under this conditions the combustion is as low as that of the low-loading Pd catalysts. Otherwise, PdO clusters are present and the combustion rate increases significantly. Finally, at higher Pd loadings (e.g., 1%) PdO clusters remain on the catalysts, even under NO-containing atmospheres, because the support capacity for stabilization is exceeded. However, when this catalyst is physically mixed with a bare acidic zeolite and exposed to NO, Pd can be transferred from a particle of

Table 1
EXAFS fitting parameters obtained on physical mixture of Pd/H-ZSM-5 and H-ZSM-5 catalysts exposed to different conditions at 500 °C. (Data taken at liquid-nitrogen temperature.)

Physical mixture	Pre-conditioning environments (500 °C)	Atomic shell	Relative coordination number (N/N_0)	Debye–Waller factor	Bond length ±0.001 (Å)	ΔE (eV)
1 wt% Pd-HZSM-5 + H-ZSM-5	$NO + CH_4 + O_2$ for 15 min	1 (Pd–O)	1.0	0.005	2.012	+3
		2 (Pd–Pd)	0.9	0.004	3.033	
		3 (Pd–Pd)	0.6	0.006	3.424	
1 wt% Pd-HZSM-5 +H-ZSM-5	NO for 20 h	1 (Pd–O)	0.7	0.002	2.062	+7
		2 (Pd–Pd)	0.1	0.003	3.128	
		3 (Pd–Pd)	0.04	0.003	3.402	

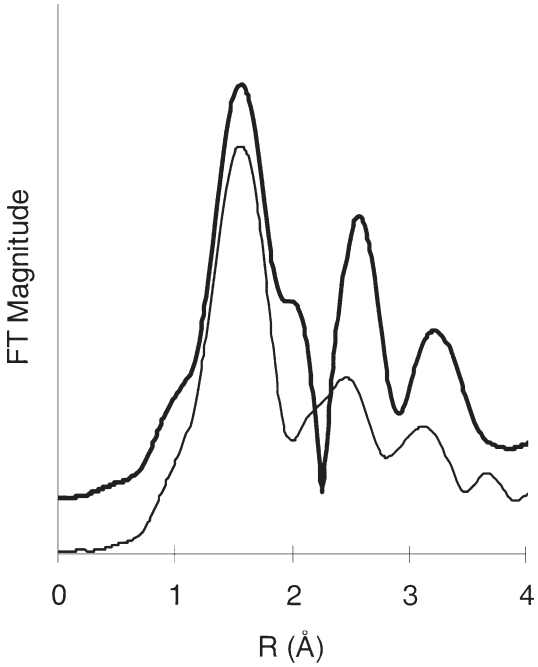

Figure 7. Fourier transform of the EXAFS data on 0.3 wt% Pd/H-ZSM-5 at liquid-nitrogen temperature after exposure to the following treatments: upper curve – reaction at 500 °C in $CH_4 + O_2$ for 2 h; lower curve – reaction at 500 °C first in $CH_4 + O_2$ for 2 h, and then in $NO + CH_4 + O_2$ (SCR) for 2 h.

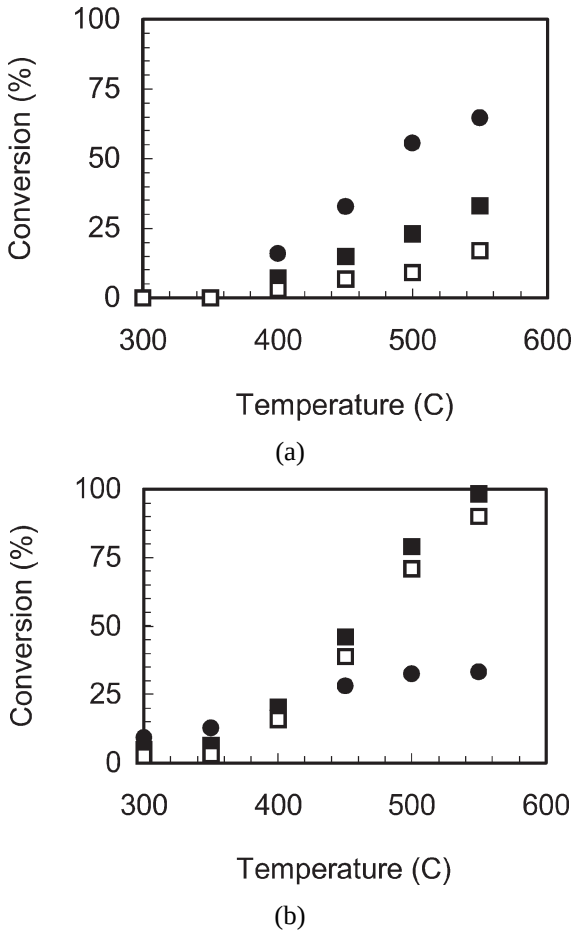

Figure 8. Methane and NO conversion as a function of reaction temperature. (•) NO conversion; (■) overall CH_4 conversion; (□) CH_4 combustion. (a) 0.3% Pd/H-ZSM-5, (b) Co/H-ZSM-5 catalyst.

over-loaded zeolite to other with anchoring sites available. Therefore, the PdO clusters present in the unselective catalysts and responsible for the high combustion activity can be eliminated, thus reducing the combustion and increasing the NO conversion.

At this point, it is important to note that, when the initially unselective catalyst (i.e., 1% Pd/H-ZSM-5 or 0.3% Pd/SiO_2) was mixed with H-ZSM-5 or H-Mor, the period of time of exposure to NO needed for the stabilization of Pd^{n+} ions was as long as 20 h, as described above. By contrast, when the unselective catalysts were mixed with sulfated zirconia, the increases in selectivity were very rapid (about 5–15 min) and remained unchanged with time on stream.

The observed behavior suggests that this transfer is much slower when the mixture involves zeolitic materials such as H-ZSM-5 or H-Mor than when it involves a non-microporous material such as sulfated zirconia. If this transfer occurs via a mobile (or volatile) $PdNO_x$ species, it is reasonable to expect that this species may get anchored near the mouth of the zeolite channels, blocking the path for additional transfer. As a result, the total elimination of PdO clusters would require a long treatment time in an atmosphere containing NO.

As shown in the EXAFS data in figure 7, we have observed that, at intermediate loadings (i.e., 0.3%), PdO clusters that are present in the absence of NO, can be converted into Pd^{n+} under SCR conditions. That is, when the catalyst is exposed to the $CH_4 + O_2$ mixture, PdO clusters appear as demonstrated by the appearance of high intensities at long coordination distances. However, when the same catalysts, after the $CH_4 + O_2$ reaction is exposed to the SCR mixture ($NO + CH_4 + O_2$) Pd^{n+} ions are formed, as evidenced by the absence of high intensities in the region corresponding to second and third coordination shells (lower curve). These morphological changes due to the presence or absence of NO are mainly responsible for the cyclic behavior of the methane combustion illustrated in figure 4.

The reversible interconversion between highly selective Pd^{n+} ions and totally unselective PdO clusters may give forth interesting possibilities. Although we do not know yet the minimum NO concentrations required to stabilize the Pd^{n+} ions, one may recognize that at high enough conversions, at the end of the catalyst bed, the Pd^{n+} ions may not longer be stabilized and the catalyst will become unselective. For example, a converter could be designed such that it converts the NO in the front part of the reactor, where the selective Pd^{n+} ions are stabilized. After the NO concentration becomes too low to stabilize the Pd^{n+} ions, the bed will contain PdO clusters which are very active for CH_4 combustion. This fraction of the bed would be used to eliminate the unreacted CH_4, which is an undesired greenhouse emission gas. The reactor would self-adjust for changes in NO concentration because the unselective PdO clusters would only appear when the NO has been eliminated.

To further ponder the potential of Pd-based catalysts, we have compared the activity and selectivity of a 0.3% Pd/H-ZSM-5 and an ion-exchanged Co-ZSM-5 catalyst, prepared according to the method described in the literature [6]. The comparison is made in figure 8 (a) and (b), which show the CH_4 and NO conversions obtained on both catalysts as a function of temperature at a GHSV of 15 000 h^{-1} after 60 min on-stream. The following feed composition was used: 3 200 ppm NO, 6 400 ppm CH_4, and 2.5% O_2, with the balance He. Under these conditions, Pd/H-ZSM-5 appears as a better catalyst than Co-ZSM-5, with a higher NO reduction activity, and most remarkably, a much higher selectivity. In separate experiments, we have also found that the 0.3% Pd/H-ZSM-5 exhibits a lower drop in activity in the presence of 10% H_2O than a comparable Co/H-ZSM-5 catalyst. This higher tolerance to water of Pd over Co-catalysts has also been reported by Ogura et al. [26].

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