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NO reduction by CH_4 in the presence of excess O_2 over Pd/sulfated zirconia catalysts

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Abstract

The selective catalytic reduction (SCR) of NO by methane in the presence of excess oxygen has been studied on a series of Pd catalysts supported on sulfated zirconia (SZ). This support is not as sensitive to structural damage by steaming as the acidic zeolites, such as H-ZSM-5 and H-Mor. In previous studies, it was shown that this type of acidic zeolites are able to stabilize Pd^{2+} ions and promote high SCR activity and selectivity, which are typically not seen in Pd catalysts. In this contribution, it has been demonstrated that SZ is able to promote the NO reduction activity in a similar way to the acidic zeolites, by stabilizing Pd^{2+} ions that is selective for NO reduction. As in the case of acidic zeolites, the stabilization of Pd^{2+} ions can occur through a transfer of Pd species from particle to particle. One of the attractive features of Pd/SZ catalysts is that they are less sensitive to water and SO_2 poisoning than Pd/H-ZSM-5 catalyst and exhibit higher reversibility after removal of water or SO_2. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: NO reduction; Sulfated-zirconia; Water and SO_2 poisoning; Pd^{2+} stabilization; FTIR of adsorbed NO

1. Introduction

One of the main obstacles for the utilization of methane as a reductant for the catalytic NO conversion in lean mixtures is its low selectivity towards the reaction with NO in competition with O_2 [1,2]. This problem is particularly important with metals such as Pd, which are very active for the total oxidation of methane [3]. Nonetheless, in recent years, some Pd catalysts have been found to be highly selective in the presence of excess oxygen (i.e. $[O_2]/[CH_4] > 2$). Several authors [3–7] have shown that when Pd is supported on acidic materials it can be active for the selective reduction of NO with CH_4. By using EXAFS [8], we demonstrated that the morphology of the Pd species, under SCR reaction conditions, strongly depends on both, 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 non-acidic materials, the Pd particles are transformed into PdO clusters, which have high activity for methane combustion [9]. We have ascribed the high selectivity exhibited by the low-loading Pd catalysts supported on acidic materials to the stabilization of the Pd^{2+} ions. Supporting evidence for the stabilization of Pd^{2+} ions on H-ZSM-5, in the presence of NO_x, has been independently found in recent TPR [10] and FTIR [11] studies as well as in DFT theoretical calculations [12]. The stabilization of Pd^{n+} ions by Brønsted sites of acidic zeolites has been proposed in many studies [13], but its role in the SCR reaction has only recently been addressed [7–11]. The FTIR investigation mentioned above [11] demon-

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strated that, although the H-ZSM5 zeolite can stabilize a small amount of Pd under O_2, the redispersion under NO is much more effective and a larger amount of Pd can be stabilized. We have shown earlier [14] that, in the presence of NO, the combustion activity of Pd/H-ZSM-5 and Pd/H-Mor is drastically inhibited and this inhibition is, at least, partially responsible for the observed enhancements in selectivity.

A major drawback of H-ZSM-5 zeolite catalysts, that prevents their practical applications in SCR, is the high sensitivity of these materials to the presence of steam at high temperatures. Under typical exhaust conditions, the structure of H-ZSM-5 is known to collapse by dealumination, causing irreversible activity losses. Hall et al. [15,16] have pointed out that H_2O attacks preferentially the Brønsted sites in the zeolite, starting the dealumination process. Therefore, acidic zeolites are particularly unstable under exhaust conditions. This characteristic is specially problematic for Pd-based catalysts since, as mentioned above, they can only be selective when Pd^{2+} ions are stabilized by the Brønsted sites of the zeolites. We are interested in exploring the possibility of using a non-zeolitic support that may not suffer the structural damage of the H-ZSM-5, while still retaining its ability to promote SCR selectivity. In previous work [3], we reported that Pd supported on sulfated zirconia exhibited high NO reduction activity in the presence of 2.5% O_2. In the present contribution, we have further investigated the catalytic performance of Pd/SZ catalysts under dry conditions and in the presence of water and SO_2. At the same time, we have characterized the interaction of these catalysts with NO and correlated this behavior with the catalytic activity.

2. Experimental

A series of Pd catalysts supported on sulfated zirconia (SZ) were studied in comparison to those supported on H-ZSM-5 and SiO_2, previously investigated [3]. The SZ support obtained from MEI had a nominal sulfate content of 9.9 wt%. A series of SZ supports with varying nominal sulfate content were prepared from a $Zr(OH)_4$ precursor (BET area 180 m^2/g, pore volume 0.28 cm^3/g). After drying the $Zr(OH)_4$ for at least 4 h at 110°C, sulfate was introduced into the solid by incipient wetness impregnation using aqueous $(NH_4)_2SO_4$ solution, and further dried at 110°C overnight. The supports were then calcined at 600°C for 4 h under ambient conditions.

The Na-ZSM-5 (Zeocat Pentasil PZ-2/54 Na, $SiO_2/Al_2O_3 = 24.3$) was obtained from Chemie Uetikon. Subsequently, it was ion exchanged with a 2.25 M NH_4Cl solution in a ratio of 20 cm^3/g zeolite, 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. Finally, to obtain the final H-ZSM-5, a thin cake of the sample was heated up to 550°C for 30 min and then treated at 550°C for two hours in flowing nitrogen. Silica (T1571, BET area 130 m^2/g) was obtained from United Catalysts and used as received.

Varying Pd loadings were accomplished by the incipient wetness impregnation method using aqueous solutions of a Pd salt (Pd $(NO_3)_2 \times H_2O$, 40.53% Pd, Alfa Aesar). The liquid/solid ratio to obtain incipient wetness was determined for each support and ranged from 0.4 to 0.7 cm^3/g. The amounts of Pd and S on fresh and used samples were determined by the ICP and LECO methods, respectively, at Galbraith Laboratories. After heating in He at 500°C, the 0.1% Pd/SZ catalyst prepared with the MEI SZ support had a surface area of 103 ± 5 m^2/g.

The catalytic activity measurements were conducted in a quartz tube reactor using 0.15–0.2 g of catalyst which, depending on the bed density (0.5 g/cm^3 for zeolites, 1.4 g/cm^3 for the SZ), resulted in GHSV ranging from 10 000 to 40 000 h^{-1}. Most runs were conducted at 500°C, using the following feed composition ranges: 3600–4800 ppm NO, 7500–9700 ppm CH_4, and (1.9–2.5)% O_2. In all cases, the O_2/CH_4 ratio was kept at 2.5. For one run, the O_2 concentration was increased to 4.8%, at a O_2/CH_4 ratio of 5.

Prior to each experimental run, the catalysts were pretreated in situ by heating in ultra-high-purity He from room temperature to 500°C at a heating rate of 5°C/min. The products and reactants were analyzed by gas chromatography using a Molsieve 5 Å capillary column. The activity results are reported as conversion of NO to N_2, based on N_2 production. To confirm that this method corresponds well with the overall NO consumption, selected runs were conducted using a

GC-MS equipped with a Porabond Q PLOT column, which allows for separation and detection of N_2O and NO. The NO consumption values, obtained through this analysis, were essentially identical to those based on N_2 production and the only by-product observed in very small quantities (i.e. <8 ppm) was N_2O.

The DRIFTS absorption spectra of adsorbed NO were obtained on a Bio-Rad FTS-40 spectrometer, equipped with an MCT detector and a diffuse reflectance cell from Harrick type HVC-DR2 with ZnSe windows. For each IR spectra, taken at a resolution of 8 cm^{-1}, 128 scans were added. The TPD of adsorbed NO were obtained on samples heated in He at 5°C/min from room temperature to 500°C, thereafter in 1% NO/He at that temperature. After 30 min, the samples were cooled in the NO/He mixture to room temperature. Then, they were purged with He at room temperature before starting a heating ramp of 10°C/min. The desorbing species were monitored with a PPT quadrupole residual gas analyzer from MKS.

3. Results

3.1. Catalytic performance of Pd/SZ compared to Pd/H-ZSM-5

In agreement with our previous findings [3], we report here that sulfated zirconia exhibits a promoting effect for the SCR activity of Pd comparable to that of the protonic zeolites H-ZSM-5 and H-Mor. Also, in line with the behavior displayed by the Pd/H-ZSM-5 catalysts, it was found that the NO reduction activity is a strong function of the Pd loading, exhibiting a maximum at a relatively low Pd wt%.

As compared in Fig. 1, the activity maximum for the Pd/SZ catalysts occurred at a much lower Pd loading (ca. 0.1 wt%) than for the Pd/H-ZSM-5 series (ca. 0.3 wt%). This result indicates that the saturation capacity of the SZ to stabilize the active species is lower than that of the H-ZSM-5 zeolite, but, at the same time, at low Pd concentrations (i.e. 0.1 wt% Pd) the NO reduction activity of Pd/SZ catalyst is higher than that of Pd/H-ZSM-5. This would be a practical advantage of Pd/SZ over Pd/HZSM-5, since higher conversions could be obtained with less Pd. Also, since the SZ support is much denser than the zeolite, the same amount of the former results in much higher GHSV than that of the latter.

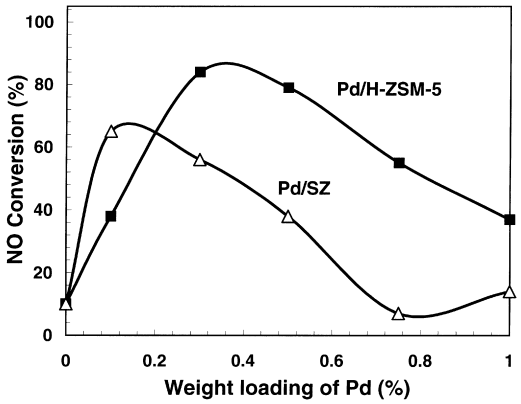

Fig. 1. NO conversion as a function of Pd loading on H-ZSM-5 and sulfated zirconia (SZ). Reaction conditions: 500°C, 0.16 g catalysts. Feed composition: 4800 ppm NO; 9700 ppm CH_4; and 2.5% O_2, balance He. Since the bed density for each support is different, the GHSVs are: 40 000 h^{-1} for Pd/SZ and 10 000 h^{-1} for Pd/H-ZSM-5.

The next comparison that we have made is on the ability of the support to suppress the undesired CH_4 combustion side reaction. As summarized in Table 1, on the H-ZSM-5 support, the 0.1% Pd catalyst presented low combustion activity, even in the absence of NO. The 0.3% Pd catalyst had a high combustion activity in the absence of NO, but it drastically decreased when NO was introduced. As mentioned above, the suppression of combustion is due to the stabilization of Pd^{2+} ions, and in the presence of NO, a larger fraction of Pd can be stabilized as Pd^{2+} than in the presence of O_2 alone [11,14]. On SZ, the 0.1% Pd catalyst had a high combustion activity without NO, but it was much lower in the presence of NO, similar to the 0.3% Pd/H-ZSM-5. However, the 0.3% Pd/SZ did not show any decrease in CH_4 combustion in the presence of NO. This difference between H-ZSM-5 and SZ in the ability to suppress the combustion on catalysts with intermediate loadings of Pd (e.g. 0.3 wt%) may be ascribed to the different saturation capacity of each support for Pd^{2+} ion stabilization.

On the Pd catalysts previously investigated [3], an increase in oxygen concentration resulted in decreasing selectivity toward NO reduction. Although this suppression is also observed on the Pd/SZ catalysts, its relative magnitude is small compared to that on Pd/H-ZSM-5 zeolites. For example, as shown in Table 1, for the 0.1% Pd/SZ, by doubling the oxygen partial pressure from 2.5 to 5%, the NO reduction was

Table 1
NO reduction and methane combustion activities of Pd catalysts under $NO + CH_4 + O_2$ (SCR) and $CH_4 + O_2$

	Time-on-stream (h)	NO conversion (%) (under $NO + CH_4 + O_2$)	CH_4 combustion (under $NO + CH_4 + O_2$) (%)	CH_4 combustion (under $CH_4 + O_2$) (%)
0.1% Pd/ $SO_4^=ZrO_2$ (SZ)[a]	2	53	35	58
0.3% Pd/ $SO_4^=ZrO_2$ (SZ)[a]	2	18	87	75
0.1% Pd/ $SO_4^=ZrO_2$ (SZ)[b]	110	56	24	–
0.1% Pd/ $SO_4^=ZrO_2$ (SZ)[c]	2	40.3	30.2	–
0.1% Pd/H-ZSM-5[d]	2	39	12	10
0.3% Pd/H-ZSM-5[d]	2	74	34	60

[a] Reaction conditions: 500°C; 41 000 GHSV; 7400 ppm CH_4; and 1.9% O_2; balance He, with or without 3600 ppm NO.
[b] Average conversion: 500°C; 40 000 GHSV; 4800 ppm NO; 9700 ppm CH_4; and 2.5% O_2; balance He.
[c] Same conditions as in 'a', except under 5% O_2.
[d] Same conditions as in 'b', except 10 000 GHSV.

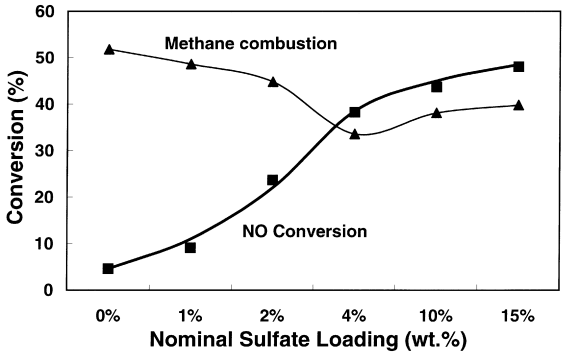

Fig. 2. NO conversion and CH_4 combustion as a function of nominal sulfate loading on 0.1 wt% Pd/SZ catalysts. Reaction conditions: 500°C, 40 000 GHSV. Composition: 3600 ppm NO; 7400 ppm CH_4; and 1.9% O_2, balance He.

only suppressed by 18%, while the methane combustion increased by 10%. On the other hand, on the 0.3% Pd/HZSM-5, such increase in O_2 partial pressure resulted in a suppression of NO conversion of 40%.

We have studied the effects of varying the amount of sulfate incorporated onto the support during the catalyst preparation. Fig. 2 shows the variation of NO conversion and methane combustion as a function of the nominal sulfate concentration impregnated on the support.

Several points are immediately obvious. First of all, the presence of sulfate on the catalyst is essential for NO reduction activity. The unsulfated Pd/ZrO_2 catalyst resulted in <5% NO conversion and a very high methane combustion activity. As the amount of added sulfate increased, the NO conversion and selectivity rapidly increased. However, beyond ca. 5 wt% sulfate, the change in activity and selectivity was less pronounced. It is known that, at 500°C, sulfate is stable on SZ under air, but it can be lost in reducing atmosphere, or even under He [17]. Therefore, we have analyzed the amount of sulfate left on the catalysts after the high temperature reaction (500°C) in a low oxidizing atmosphere. The sulfate analysis indicated that the amount left on the most active catalysts (i.e. those prepared with 10 and 15 wt% nominal sulfate) was about 2.9 wt% after 6 h reaction. As seen in Fig. 2, it appears that this sulfate loading represents a critical value since below this loading the NO reduction activity is almost linearly proportional to the nominal sulfate concentration. In this range, most of the sulfate loaded initially is retained on the zirconia surface.

These results demonstrate that the presence of sulfate is essential in promoting the selectivity enhancement, possibly by providing anchoring sites for Pd^{2+} ions. It is known that SZ contains strong Brønsted sites that may act as those of the zeolite in the stabilization of Pd^{2+} ions. As the sulfate loading increases, the density of Brønsted sites may increase, reaching a saturation below the capacity for sulfate uptake. The excess sulfate, loaded on the zirconia, is more labile and can be easily lost as SO_2 during calcination [18,19].

The observed sulfate losses may raise questions about the long-term stability of these SZ catalysts. Therefore, we have conducted reaction measurements for a 110-h period on the 0.1% Pd/SZ catalyst, prepared using the commercial MEI SZ support which has an initial nominal sulfate content of 9.9%. Two important points were observed on this long run. First of all, the NO conversion and SCR selectivity did not

decrease during this period. Second, the residual sulfate on the sample after 110 h on-stream was 4.9 wt%, compared to the same sample after 2 h on-stream, 5.9 wt%. Since this 17% loss of sulfate did not result in any suppression of activity or selectivity, we may infer that there exists a large excess of sulfate that does not participate in the reaction or in the stabilization of the Pd^{2+} species.

The fact that a significant amount of sulfate groups are lost, and the catalyst still keeps an NO conversion comparable to that of a 0.2% Pd/H-ZSM-5, deserves further attention. The maximum possible amount of Brønsted sites on an SZ is equal to the amount of sulfate groups, which after pretreatment is only about 300 μmol/g (equivalent to 2.9 wt% sulfate). This number is much lower than the Brønsted sites present in H-ZSM-5 (1280 μmol/g). H-ZSM-5, without Pd, has some activity for NO reduction, but much lower than that of Pd/H-ZSM-5 [3]. Similarly, SZ alone has a very low activity, i.e. <3% NO conversion under the conditions in which 0.1% Pd/SZ exhibits around 65% conversion.

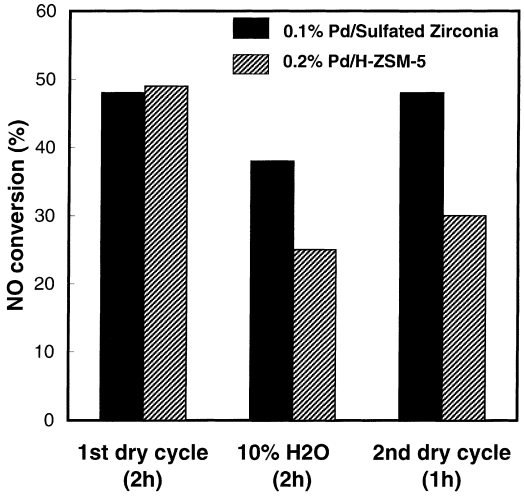

Fig. 3. Comparison of NO conversion obtained on 0.1 wt% Pd/SZ (solid bars) and 0.2 wt% Pd/H-ZSM-5 (shaded bars) at 500°C. The first set of bars represent the conversion after 2 h under dry conditions. The second set is after 2 h in the presence of 10% water. The third set is after removing the water from the feed. Reaction conditions: 0.21 g catalyst; 72 cc/min of 3600 ppm NO; 7400 ppm CH_4; and 1.9% O_2, balance He. The He flow was adjusted so the reactant concentrations were kept unchanged when H_2O was added.

3.2. Poisoning effect of water and SO_2 on Pd/SZ compared to Pd/H-ZSM-5

Perhaps, the most promising characteristics exhibited by the Pd/SZ catalysts is their stability in the presence of water or SO_2 impurities. The SZ-supported catalysts compare very favorably with other SCR catalyst in the presence of 8–10% water or 50–100 ppm SO_2 impurities. As shown in Fig. 3, when the 0.2% Pd/H-ZSM-5 and the 0.1% Pd/SZ catalysts were compared under dry conditions, they exhibited comparable NO conversions. However, in the presence of 10% water, the drop in activity for the Pd/H-ZSM-5 was more pronounced than that for the Pd/SZ. Similarly, the activity recovery, observed when removing the water from the feed after 2 h, was much greater for the Pd/SZ catalyst than for Pd/H-ZSM-5.

Likewise, the comparison of the effect of SO_2 was greatly favorable for the SZ-supported catalyst over the Pd/H-ZSM-5 catalyst. As illustrated in Fig. 4, while in the presence of 75 ppm SO_2 the Pd/H-ZSM-5 catalyst lost almost 1/3 of its initial activity, the Pd/SZ catalyst was almost unaffected. In separate runs, it was observed that a sample of Co-ZSM-5 (70% exchange),

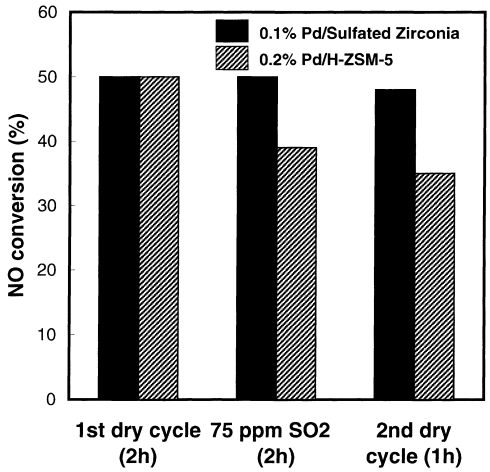

Fig. 4. Comparison of NO conversion obtained on 0.1 wt% Pd/SZ (solid bars) and 0.2 wt% Pd/H-ZSM-5 (shaded bars) at 500°C. The first set of bars represent the conversion after 2 h under clean conditions. The second set is after 2 h in the presence of 75 ppm SO_2. The third set is after removing the SO_2 from the feed. Same reaction conditions as in Fig. 3.

a typical SCR catalyst, exhibited much higher sensitivity to water and SO_2 than the Pd/SZ catalyst. Under conditions for which the Co-ZSM-5 catalyst gave an NO conversion of 50% under dry feed, it decreased to 15 and 16% in the presence of water and SO_2, respectively. In this case, as for the Pd/SZ, the activity was recovered after removing water or SO_2.

Finally, when resistance to the simultaneous presence of water and SO_2 was compared for several catalysts, the Pd/SZ exhibited a small advantage over the rest. For example, the NO conversion on the 0.2% Pd/H-ZSM-5 catalyst dropped from 50 to 20%, in the presence of 75 ppm SO_2 and 10% water. After removal of impurities, the activity partially recovered to 30% conversion. By contrast, on the 0.1% Pd/SZ, the conversion only dropped from 50 to 40% under the same conditions, but it did not recover after removal of the impurities, remaining at 40% conversion.

3.3. TPD and DRIFTS spectra of adsorbed NO on Pd/SZ catalysts

A series of TPD and DRIFTS experiments have been conducted on the Pd/SZ catalysts as well as on the SZ support and a reference Pd/SiO_2 catalyst. Fig. 5 shows the TPD profiles of the three samples

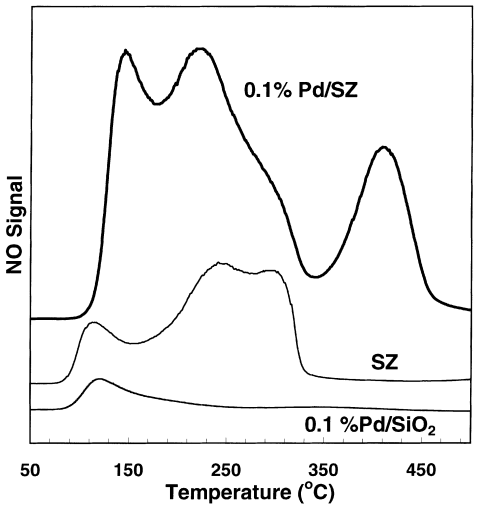

Fig. 5. Temperature-programmed desorption (TPD) of adsorbed NO on 0.1 wt% Pd/SiO_2, SZ support, and 0.1 wt% Pd/SZ. The pretreatment consisted in heating in He and then in 1%NO/He, cooling in NO/He to room temperature, purging in He, and, finally, heating at a temperature ramp of 10°C/min in 30 cc/min He flow.

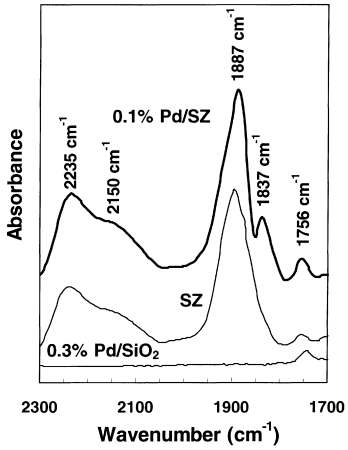

Fig. 6. Infrared spectra of 0.1 wt% Pd/SiO_2. SZ support, and 0.1 wt% Pd/SZ, taken in the presence of 5% NO/He at room temperature after heating in He up to 500°C and then cooling to room temperature. The spectrum of each sample in He at room temperature was taken as a reference spectrum. The gas-phase contribution was subtracted from each spectrum.

after the standard pretreatment. For the Pd/SiO_2 catalyst a small desorption peak was observed at low temperatures and the overall integrated area corresponded to only 0.3 μmol/g. The SZ support exhibited a much higher NO adsorption capacity (2.7 mmol/g) with desorption peaks at 120, 250, and 300°C. Interestingly, the adsorption capacity determined for the 0.1% Pd/SZ (6.7 μmol/g) was much higher than the sum of those for the 0.1% Pd/SiO_2 and SZ, but comparable to the total amount of Pd (9.3 μmol/g) present in the catalyst.

The trends observed by TPD correlated well with the DRIFTS results. Fig. 6 shows the IR absorbance spectra of adsorbed NO at room temperature on the three samples in the region 1700–2300 cm^{-1}, obtained after pretreating the samples in He at 500°C. It is observed that the Pd/SiO_2 presented a very weak band centered at ca. 1743 cm^{-1}. This band has been previously observed by other authors [20] and has been ascribed to NO adsorbed on metallic Pd.

In line with the TPD results, the SZ sample exhibited a much higher NO adsorption capacity than Pd/SiO_2, with bands at 2239, 2150, 1898, and 1756 cm^{-1}. Finally, the Pd/SZ catalyst exhibited peaks similar to those of the SZ support. In addition, this spectrum presented a clear new feature at 1837 cm^{-1}. Evidently, the bands in the range 2000–2300 cm^{-1} are not associated with Pd species, but with NO species

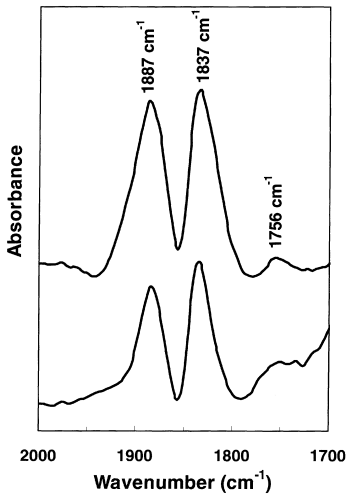

Fig. 7. Upper line: difference spectrum of the two spectra shown in Fig. 6: NO adsorbed on SZ subtracted from NO adsorbed on Pd/SZ in 5% NO/He. Lower line: infrared spectrum on the Pd/SZ sample, after purging in He for 30 min at room temperature.

adsorbed on acid sites of the support. Bands in this region, previously observed for the adsorption of NO on acidic zeolites, have been assigned to either NO^{2+} or NO^{+} associated with acidic hydroxyls [21–23]. We will concentrate on the analysis of the bands at 1887 and 1837 cm^{-1}.

To separate the contributions of NO adsorbed on Pd from that of NO adsorbed on SZ, a difference spectrum was obtained by subtracting the spectrum corresponding to SZ from that of Pd/SZ. This is shown in Fig. 7, which also includes the spectrum obtained on Pd/SZ after purging in He for 30 min. at room temperature. Since this purging removes the weakly adsorbed NO, the almost perfect correspondence between the two spectra indicates that the NO adsorbed on the Pd species are the most strongly held on the surface.

It is clear that, not only the band at 1837 cm^{-1}, but also that at 1887 cm^{-1}, are associated with Pd species stabilized by the support. These bands are not present for either Pd/Silica or the SZ support. It is interesting to note that bands at approximately these frequencies have been observed in previous work for the adsorption of NO on Pd/H-ZSM-5 [11,24] and other acidic zeolites [7]. The appearance of these bands in Pd/SZ would indicate that SZ is able to stabilize Pd species of the same nature as those stabilized by the acidic zeolites. Bell et al. [11,12] proposed that Pd^{2+} ions were stabilized by more than one H^{+} in H-ZSM-5. In parallel to that idea, we could propose that, on SZ, the Pd^{2+} are stabilized by protons associated with surface SO_4 groups. DRIFTS spectra of 0.1% Pd/SZ show the presence of residual sulfate left on the surface with absorption bands at 1043, 1197–1308, and 1396 cm^{-1}. These bands correspond to ν_{S-O} stretching mode of all surface sulfate species, symmetric O=S=O stretching mode of $(Zr)_2SO_2$, and asymmetric O=S=O stretching mode of $(ZrO)_2SO_2$ species, respectively [25].

3.4. Catalytic performance of (Pd/SiO_2+SZ) physical mixtures

In a previous work [3], we observed that well mixed physical mixtures of Pd/SiO_2 and sulfated zirconia powders exhibited high NO reduction activity. This was a surprising result since each component alone was ineffective. Pd/SiO_2 was totally unselective and SZ was almost inactive. More recently, our EXAFS results [14] showed that, while on 1% Pd/H–Mor catalysts PdO clusters remained on the catalyst after treatment in NO, when this catalyst was physically mixed with excess H-Mor and exposed to NO at 500°C for 20 h a total redispersion and stabilization of Pd^{2+} ions occurred, most probably involving transfer of Pd species from one support particle to the other. While in the case of zeolites, the period of time of exposure to NO needed for the stabilization of Pd^{2+} ions was as long as 20 h, the mixtures with sulfated zirconia only needed a very short exposure to NO at 500°C. We have explained this difference in terms of a much slower transfer and stabilization process when a microporous material is involved [14].

We have investigated the stabilization process that takes place in these physical mixtures. Fig. 8 shows the NO reduction and methane combustion activities of a 1 : 1 physical mixture of 0.1% Pd/SiO_2 + SZ, which contained the same amounts of Pd and SZ as that of the 0.1% Pd/SZ catalyst. When the mixture was pretreated in 5% O_2/He at 500°C, the subsequent methane combustion activity in $CH_4 + O_2$ was relatively high and slightly increased as a function of time. This is a typical behavior of Pd supported on SiO_2 under methane combustion conditions [9]. When NO was incorporated in the reaction mixture, the NO reduction conversion slowly increased from essentially zero until

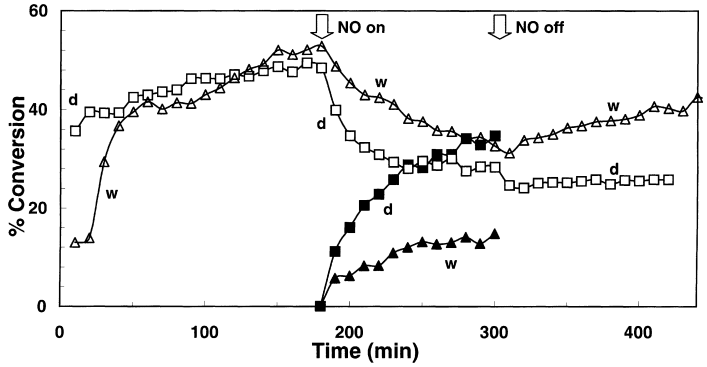

Fig. 8. NO conversion (full symbols) and methane combustion (open symbols) over a physical mixture of 1 : 1 (by weight) 0.1% Pd/SiO_2 and SZ, pretreated under $5\%O_2$/He (squares, line d) or 10% $H_2O/5\%O_2$/He (triangles, line w). Reaction periods: 0–180 min $CH_4 + O_2$, 180–300 min SCR ($NO + CH_4 + O_2$), and 300–420 min in $CH_4 + O_2$. Reaction conditions: 500°C; 40 000 GHSV; 7400 ppm CH_4; 1.9% O_2; balance He, with or without 3600 ppm NO.

reaching ca. 50%. During this process, the methane combustion continuously decreased. As we have explained in our previous work [14], these changes are due to the transfer of Pd species from the SiO_2 particles to the SZ particles, where Pd is converted from a combustion catalyst on the former to an SCR catalyst on the latter. As mentioned before, the redispersion process is time-dependent and varies with the type of supports used. In this case, after exposure to $CH_4 + O_2$, the redispersion process took ca. 100 min. before the NO reduction activity reached its steady-state. When NO was removed from the gas phase, the combustion activity was much lower than it was during the first run in $CH_4 + O_2$. This is because the combustion activity of Pd on SZ is lower than on SiO_2.

To study the effects of water vapor on the transfer of Pd species, the same reaction cycle was then conducted on a physical mixture which was pretreated at 500°C in O_2/He containing 10% H_2O. This time, the methane combustion activity started at a very low value, but increased to the same final conversion as that reached with the mixture treated in dry He. This behavior can be explained by the presence of H_2O adsorbed on Pd, which is known to inhibit methane combustion. As the reaction proceeded and water was removed from the surface, the activity reached the same level as in the 'dry' cycle. The most important difference was observed when NO was incorporated into the feed. This time, the increase in NO conversion and decrease in combustion were much less pronounced than for the 'dry' cycle. This result suggests that the water incorporated during the 'wet' pretreatment blocked the sites on the SZ responsible for the stabilization of Pd^{2+} ions. As a result, the transfer and stabilization was not as effective as in the 'dry' cycle. In agreement with this view, the combustion level resulting after removal of NO, was this time significantly higher and close to the level that the mixture had before exposure to NO.

The foregoing comparison has shown that water can interfere in the process of stabilization of Pd species on the SZ support. To study the effect of water after stabilization had taken place, a similar physical mixture was first exposed to reaction conditions ($NO + CH_4 + O_2$) at 500°C for 2 h. During this period, the Pd transfer is supposed to occur. Subsequently, 10% H_2O was incorporated into the feed. After 2 h, the water was removed. The resulting NO conversion before (bar a), in the presence of water (bar b), and after the water was removed (bar c) are summarized in Fig. 9. The drop in activity in the presence of water and the activity recovery after removal of water observed on this physical mixture are very similar to those observed on the 0.1% Pd/SZ catalyst (compare with Fig. 3). To compare the effect of pretreating in water before, and after, the transfer of Pd onto the SZ, Fig. 9 includes the NO conversion (bar d) on the physical mixture exposed to the 'wet' pretreatments, and then run without water. This value was taken from the steady-state value in Fig. 8 (curve w). It is clear that the effect of water is more pronounced and irreversible over the SZ before Pd^{2+} has been

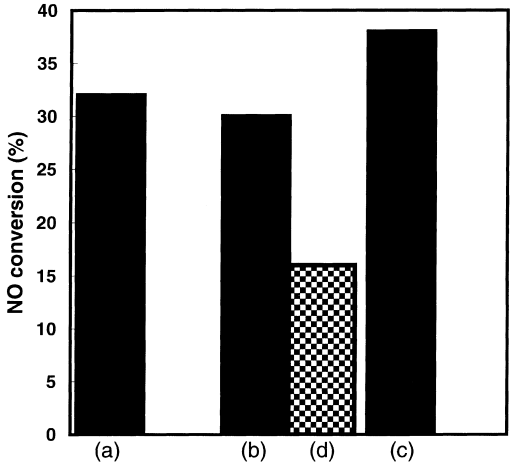

Fig. 9. NO conversion on a physical mixture of 1 : 1 (by weight) of 0.1% Pd/SiO_2 and SZ during (a) first dry SCR cycle (2 h), (b) SCR with 10% water (2 h), and (c) second dry SCR cycle (2 h). NO conversion on the same mixture under dry SCR, but after pretreatment under 10% H_2O/He prior to reaction (d). Reaction conditions: 500°C; 40 000 GHSV; 7400 ppm CH_4; and 1.9% O_2; balance He, 3600 ppm NO.

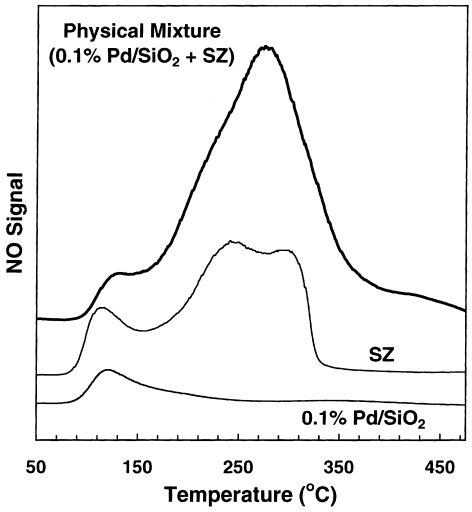

Fig. 10. Temperature-programmed desorption (TPD) of adsorbed NO on a physical mixture of 1 : 1 (by weight) of 0.1 wt% Pd/SiO_2 and sulfated zirconia (SZ). The pretreatment was the same as that indicated in Fig. 5. The TPD profiles of the two individual components are also shown.

stabilized. It can be seen that, after the stabilization of Pd^{2+}, the activity loss is fully reversible. Therefore, in this case, water may only block sites reversibly.

3.5. TPD and DRIFTS spectra of adsorbed NO on (Pd/SiO_2+SZ) physical mixtures

In addition to the catalytic activity measurements, we have conducted TPD and IR characterization studies on the physical mixtures of Pd/SiO_2 and SZ powders to show that this transfer indeed takes place and that SZ is able to anchor and stabilize highly dispersed Pd species, in a similar way as the acidic zeolites.

Fig. 10 shows the TPD profile of the physical mixture (Pd/SiO_2 + SZ) after the standard pretreatment. According to the previous results, a transfer of Pd from SiO_2 to SZ should have taken place and the TPD should resemble that of Pd/SZ catalyst rather than the simple addition of the profiles of Pd/SiO_2 and SZ. The TPD profiles corresponding to the individual components of the mixture are included for comparison. Two important differences can be observed between the physical mixture and the individual components. First of all, the NO adsorption capacity of the mixture was significantly greater than the sum of the capacities of the two components. Also, the physical mixture exhibited NO desorption at temperatures significantly higher than those of any of the two components, similar to those of the Pd/SZ.

In combination with the TPD results, the IR studies of the physical mixture definitely demonstrated that Pd species are transferred from the SiO_2 to the SZ support. The DRIFTS spectra of adsorbed NO on the physical mixture (Pd/SiO_2 + SZ) after 500°C pretreatments in either He or 5% NO/He are shown in Fig. 11. For comparison, the spectra corresponding to 0.3% Pd/SiO_2 and 0.1% Pd/SZ after the same treatments are included in the figure. Aside for a slight frequency shift possible due to oxidation of Pd, the spectrum for the Pd/SiO_2 catalyst did not change significantly after the high-temperature pretreatment in NO. Similarly, the spectrum for the 0.1% Pd/SZ was not altered by this pretreatment. However, an important change was observed for the physical mixture. After heating in He, the spectrum for the physical mixture was simply the addition of the bands corresponding to NO on Pd/SiO_2 and NO on SZ. However, after heating in NO, the resulting spectrum was very similar to that of Pd/SZ, with the characteristic band at 1837 cm^{-1} indicating the presence of Pd species stabilized by the SZ support.

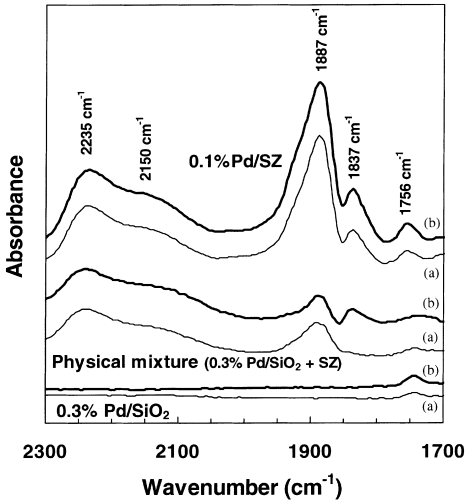

Fig. 11. Infrared spectra of a physical mixture of 1 : 1 (by weight) of 0.3 wt% Pd/SiO_2 + SZ, SZ support alone, and 0.3% Pd/SiO_2 taken in the presence of 5% NO/He at room temperature following (a) heating to 500°C in He, and (b) heating to 500°C in 5% NO/He. The spectrum of each sample in He at room temperature was taken as reference. The gas-phase contribution was subtracted from each spectrum.

Table 2
NO reduction activity compared to the amount of irreversible NO adsorbed (determined from NO TPD) on various samples[a]

Sample	NO conversion (%)	NO adsorption (μmol/g_{cat})
0.1%Pd/SiO_2	0	0.30
0.3%Pd/H-Y	10	0.98
$SO_4^=ZrO_2$ (SZ)	3	2.65
Physical mixture (0.1%Pd/SiO_2 + $SO_4^=ZrO_2$(SZ))	45	4.34
0.1%Pd/ $SO_4^=ZrO_2$ (SZ)	60	6.73
0.3%Pd/H-ZSM-5	85	19.90
0.3%Pd/H-MOR	80	47.2

[a] Reaction conditions: 500°C; 0.16 g catalysts; total flow 53.3 cm^3/min. Feed composition: 4800 ppm NO; 9700 ppm CH_4; and 2.5% O_2; balance He.

We have found that a necessary, but not sufficient, condition for NO reduction activity is the ability of the catalyst to adsorb NO. As illustrated in Table 2, active catalysts exhibit high NO adsorption capacity, but some materials can adsorb NO and still remain inactive or unselective. For example, catalysts such as Pd/HY or Pd/SiO_2, which had no SCR activity, were not able to adsorb significant amounts of NO. In parallel with the NO adsorption capacity, the activity greatly increased for 0.1% Pd/SZ, 0.3% Pd/H-ZSM-5, 0.3% Pd/H-Mor, and even for the physical mixtures Pd/SiO_2 + SZ.

By contrast, H-ZSM-5 adsorbs significant amounts of NO, but it is not very active for SCR. Brønsted sites may be responsible for a significant fraction of NO adsorption. However, these sites have a much lower catalytic activity than Pd^{2+} sites. The rate may be only a function of the density of stabilized Pd^{2+} ions, able to adsorb NO. Similarly, bare ZrO_2 can strongly adsorb NO, perhaps forming a surface nitrate compound. However, bare ZrO_2 is totally inactive for SCR. The addition of sulfate to ZrO_2 significantly reduces the adsorption of this inactive NO species, while addition of Pd to SZ increases the NO adsorption again, but this adsorption does result in an active species which is most probably related to the Pd^{2+} sites.

Other Pd catalysts that adsorb NO but are not selective for NO reduction are those with Pd loadings higher than the saturation capacity of the support to stabilize Pd^{2+} ions. For example, the 0.3 wt% Pd/SZ has an NO adsorption capacity similar to that of the 0.1 wt% Pd/SZ. However, the NO reduction activity of the latter was significantly higher than that of the former. In fact, the NO adsorption capacity of 0.3% Pd/SZ was 7.6 μmol/g while that of the 0.1% Pd/SZ was 6.7 μmol/g. However, if these numbers are expressed per Pd atom they would be 0.27 and 0.72, respectively. Thus, these NO/Pd numbers show that a large fraction of the Pd is in the form of Pd^{2+} ions on the 0.1% Pd/SZ, while on the 0.3% Pd/SZ, they are in the form of PdO clusters, which are active for combustion. Therefore, although the 0.3%Pd/SZ catalyst has Pd^{2+} ions that could adsorb NO, the reductant is used up by combustion and as a result the NO reduction becomes low.

In line with these concepts, Gelin et al. [24] have found a striking correlation between the NO adsorbed on Pd^{2+} ions and the NO reduction activity. They observed that the intensity of the infrared band corresponding to NO adsorbed on Pd ions (1880 cm^{-1}) increased with Pd loading up to a given saturation point. In agreement with our previous results [3,8], they observed that further increase in Pd loading did not increment the intensity of the band and caused an increase in the methane combustion.

4. Conclusions

In this contribution, we have investigated the catalytic performance of low-loading Pd catalysts supported on sulfated zirconia (SZ). It was demonstrated that SZ is able to promote the NO reduction activity in a way comparable to the acidic zeolites. One of the benefits of this support over acidic zeolites is that it does not suffer the structural damage that is normally associated with dealumination by steaming. One of the common problems of sulfated zirconia catalysts is the loss of sulfate, which in the case of acid-catalyzed reactions causes activity losses. In this case, sulfate losses do occur, but the small residual sulfate concentration remaining on the catalyst is enough to sustain high NO reduction activity.

The 0.1 wt% Pd/SZ was less sensitive to water and SO_2 poisoning than Pd/H-ZSM-5 catalyst with a per-gram comparable initial activity. Also, the SZ-supported catalyst exhibited a higher reversibility of activity after removal of water or SO_2.

Like the acidic zeolites, SZ promotes the SCR activity of Pd by stabilizing Pd^{2+} ions, which are able to adsorb NO strongly enough to participate in the high-temperature reaction. As in the case of acidic zeolites, the stabilization of Pd^{2+} ions can occur through inter-particle transfer, since it was shown that when physical mixtures of $Pd/SiO_2 + SZ$ were pretreated in NO, the transfer of Pd species and stabilization of Pd^{2+} ions onto the SZ readily occurred.

Acknowledgements

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