Sulfated zirconia and tungstated zirconia as effective supports for Pd-based SCR catalysts

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Abstract

It is now well established that even though Pd supported on acidic zeolites is highly selective for CH_4-SCR, zeolitic structures are susceptible to dealumination under hydrothermal environments. In this contribution, we have investigated the ability of non-zeolitic acidic materials to promote the SCR selectivity and stability in the presence of H_2O and SO_2. The results of catalytic activity measurements and characterization tests indicate that sulfated zirconia and tungstated zirconia are supports as effective as the zeolites for the promotion of SCR activity. The high SCR activity of these catalysts can be ascribed to the formation of isolated Pd^{2+} ions on acid sites. It is proposed that the stabilization of Pd^{2+} on these supports is similar to the stabilization previously reported for acidic zeolites. The remarkable characteristic of these Pd catalysts supported on sulfated zirconia and tungstated zirconia is that when they were tested over a 40 h reaction period in the presence of H_2O and SO_2, they appeared to be significantly more resistant than zeolite-based catalysts. © 2000 Published by Elsevier Science B.V.

Keywords: Sulfated zirconia; Tungstated zirconia; SCR catalyst

1. Introduction

The performance of Pd catalysts in the selective catalytic reduction of NO by CH_4 has been found to depend on the type of support used. In the presence of excess oxygen (i.e. $O_2/CH_4 > 2$), Pd is an active catalysts for total oxidation [1], which makes it unselective for SCR. Thus, little attention was initially paid to its applications as NO reduction catalyst. However, later it was found that, when loaded at low concentrations on acidic supports, it can become selective [2]. Several authors [2–4,27] have shown that under lean conditions, acidic zeolites such as H-ZSM-5 and H-MOR are able to promote the selectivity of Pd towards NO conversion under a mixture of $NO/CH_4/O_2$.

The selectivity enhancement was ascribed to the ability of the support to stabilize Pd in the form of isolated Pd^{2+} ions through their Brønsted acid sites [5,6]. This proposal was supported by EXAFS [5], which revealed the presence of Pd^{2+} ions on a selective 0.3% Pd/H-ZSM-5 sample, with low intensities in the second coordination shell. This behavior contrasted with the non-selective catalysts such as 0.1% Pd/SiO_2 or 1% Pd/H-ZSM-5, which exhibited high intensities in the second shell region, indicating the presence of PdO clusters. It was proposed that the formation of these clusters favor the combustion of CH_4 and suppresses the NO conversion. Similarly, DRIFT studies [7] concluded that as NO was introduced to a pre-reduced Pd/H-ZSM-5 sample, metallic Pd was oxidized and redispersed into isolated species. At the same time, on the basis of the intensity change observed for an absorption band at $3610\, cm^{-1}$, ascribed to the OH stretch of Brønsted groups, these authors suggested that the

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stabilization of Pd requires a pair of Brønsted acid sites. Supporting evidence for the stabilization of Pd^{2+} ions on zeolites has also been drawn independently from TPR [8] and DFT [9] theoretical calculations.

Preceding work in this area mainly focused on acidic zeolitic supports such as H-ZSM-5 and H-MOR. Although these catalysts exhibit high NO reduction activity, they are sensitive to steaming at high temperatures [10,11]. Severe losses of Al atoms from the zeolitic framework on Pd/H-ZSM-5 upon steaming have been demonstrated by ^{27}Al-NMR [12]. Since the selectivity towards NO on Pd catalysts relies on the stabilization of Pd^{2+} on acid sites that are associated with the framework Al, dealumination under hydrothermal conditions may destabilize the Pd^{2+} ions, resulting in the conversion of selective Pd ions into agglomerated PdO, with permanent loss in activity. Therefore, despite their high activity under clean conditions, zeolite catalysts have limited value for industrial applications due to their poor performance under water.

The goal of the present work is to explore the possibility of using non-zeolitic acidic materials as supports for SCR under the presence of H_2O and SO_2 impurities. We have previously found that $SO_4^{2-}ZrO_2(SZ)$ is able to stabilize the selective Pd^{2+} species and furthermore, to exhibit higher resistance to water when compared to a Pd/H-ZSM-5 catalyst during a 2 h reaction period [13]. However, SO_4^{2-} is labile at high temperatures under reducing conditions, and may result in activity losses. A material that may be structurally more stable than SZ is the zirconia modified by tungsten oxide (WZ). This material has exhibited high activity for reactions that require strong Brønsted acid sites such as alkane isomerization and alkylation [14–17]. Since WZ is structurally more stable under reducing conditions, we have examined the deactivation behavior under H_2O and SO_2.

2. Experimental

The $SO_4^{2-}ZrO_2$ and WO_xZrO_2 supports are indicated as SZ and WZ, respectively. They were prepared by incipient wetness impregnation of zirconium oxyhydroxide ($Zr(OH)_4$ solid, from MEI) with ammonium sulfate (Mallinckrodt) and ammonium metatungstate (Aldrich) solutions, respectively, following drying at

110°C for at least 4 h. The SZ support contains 2 wt.% sulfate and the WZ support contains either 13.2 or 18 wt.% tungsten. H-Mordenite (LZ-M-8, SiO_2/Al_2O_3 ratio = 8, from UOP) was used as received. During the preparation process, H-MOR and the impregnated WZ samples were dried at 110°C overnight and calcined in flowing dry air with a ramp of 5°C/min to the desired temperature, subsequently held at that temperature. Impregnated WZ and H-MOR were held at the 650°C for 1.5 h and at 550°C for 3 h, respectively. The SZ support samples were calcined at 600°C under stagnant air in atmospheric conditions for 4 h. After calcination, all the samples were cooled and kept at 110°C prior to impregnation of Pd, which was accomplished by dropwise addition of aqueous solutions of $Pd(NO_3)_2$ (salt from Alfa Aesar) at a liquid/solid ratio corresponding to the incipient wetness point of each support. This point was determined as $0.37\,cm^3/g$ for zirconia and $0.89\,cm^3/g$ for H-MOR. For selected runs, Pd/SZ was prepared from a commercial SZ from MEI, having a nominal sulfate content of 9.9 wt.%. Two other samples, Pd/ZrO_2 and bare ZrO_2 were prepared as reference materials in the DRIFTS experiment. ZrO_2 was prepared from the $Zr(OH)_4$ precursor, dried at 110°C and calcined at 650°C. Addition of Pd on ZrO_2 followed the same procedure as described above for the other catalysts.

Prior to each activity measurement, the catalysts were pretreated in situ in He at 500°C. The reaction was then conducted at 500°C under the following feed composition: 3600 ppm NO, 7500 ppm CH_4, and 1.9% O_2 in balance He. Depending on the sample density, the GHSV ranged from 10,000 for Pd/H-MOR to 40,000 for Pd/SZ or Pd/WZ. In all cases, the O_2/CH_4 ratio was kept at 2.5. Catalyst-life studies were performed under 10 vol.% H_2O and/or 75 ppm of SO_2 at the same space velocity as that of clean conditions. The NO consumption and N_2 production were monitored by gas chromatography and GC–MS. The agreement within these values indicated that essentially all the NO converted formed N_2. Thus, the NO conversion reported here was based on N_2 production. On several samples, the N_2O production was measured and in all cases these values were very small, e.g. less than 0.8% conversion. DRIFTS experiments were performed on a Bio-Rad FTS-40 spectrometer. Each spectrum was taken at room temperature after purging in He for 30 min, following the adsorption

of 5% NO/He for 30 min at room temperature. Prior to NO adsorption, the sample was heated from room temperature to 500°C and cooled to room temperature under He. 128 scans at a resolution of 8 cm^{-1} were added to obtain the final spectrum.

3. Results and discussion

In our previous study, we showed that SZ was able to promote NO reduction [13]. An increase in sulfate concentration from 0 to 10% was paralleled by an increase in NO conversion from 4 to 49%. It is known that sulfate species tend to leach from the support, forming volatile SO_2 or H_2S under low O_2 or reducing atmospheres [18]. Numerous studies have demonstrated the presence of Brønsted acidity on SZ [19]. Therefore, we have ascribed the enhancement in selectivity observed on these SZ-supported catalysts to the presence of Brønsted acid sites on SZ support, which are able to stabilize Pd as isolated ions in a similar way as the acidic zeolites. Since the concentration of Brønsted sites determines the capability to accommodate Pd^{2+} ions and, in turns, it depends on the amount of sulfate on the zirconia support, it could be expected that sulfate leaching during reaction might result in permanent losses in selectivity.

One might expect that such a loss would be more evident on a sample with low sulfate concentration, since a sample containing sulfate in excess would keep enough acid sites to maintain the stabilization of Pd^{2+} ions. Therefore, in this contribution, we have compared the stability of two Pd/SZ catalysts containing the same Pd loading (0.1 wt.%) but with different nominal SO_4^{2-} concentrations, 2.0 and 9.9 wt.%. As illustrated in Fig. 1, these samples exhibited significant differences in selectivity from the start of the reaction, but no sign of deactivation or selectivity loss was observed as a function of time on stream over a 100-h period, indicating that the sulfate species on the surface are very stable under lean SCR reaction conditions.

Tungstated zirconia, or tungsten-oxide-modified zirconia, comprises a new class of solid acids containing tungsten dopants that are very stable even under reducing environment [20,21]. To study their potential as SCR supports, we have prepared a 0.1% Pd/WZ catalyst and tested it for the $NO/CH_4/O_2$ reaction. The NO conversion for this sample at 500°C and at a GHSV of 40,000 was found to be 51%, which compares very favorably with other SCR catalysts based on zeolite supports. For example, using the same flow rate and amount of catalyst as with the 0.1% Pd/WZ catalyst, the NO conversion on a 0.3% Pd/H-MOR was about 75%. Interestingly, the Pd/WZ catalyst, as well as the Pd/SZ, have a density four times higher than that of the zeolite catalysts. Therefore, on a bed-volume basis the GHSV used for the zirconia catalysts is four times higher. In some applications this advantage could be substantial.

We have experimental evidence for the presence of strong Brønsted acid sites on both the WZ and SZ supports, which we associate with the stabilization of Pd^{2+} ions. Both supports showed the ability of decomposing pre-adsorbed isopropylamine at around 350°C during a TPD in He, expected for solids containing Brønsted acid sites [22]. At the same time, upon NO
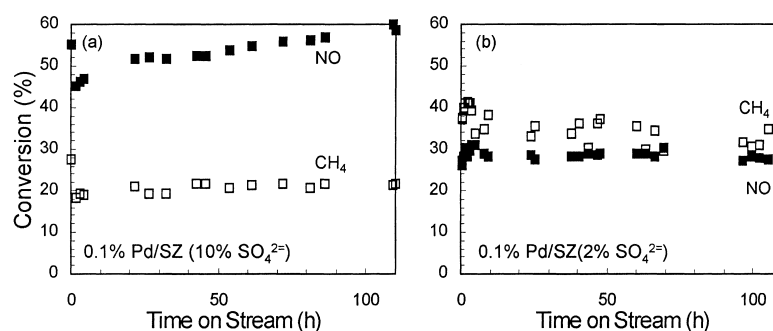

Fig. 1. NO conversion and CH_4 combustion over 0.1% Pd/SZ: (a) support with 10 wt.% SO_4^{2-}; (b) support with 2 wt.% SO_4^{2-}. Reaction conditions: 500°C, 40,000 GHSV, 3600 ppm NO, 7400 ppm CH_4, 1.9% O_2, balance He.

adsorption at room temperature, we have observed on both supports IR absorption bands at $2133 \, cm^{-1}$, which are characteristic of NO^+ species adsorbed on Brønsted sites [23].

To compare the stability of the WZ- and SZ-supported catalysts under reducing conditions at reaction temperatures, we measured the SCR activities under $NO/CH_4/O_2$ after treatment in NO/CH_4 (without O_2) and then after 1 h under H_2 flow. The NO reduction and CH_4 combustion activity after the treatments, along with the steady state activity, depicted in Fig. 2, indicated a slight decrease in NO conversion on both samples after the NO/CH_4 treatment. At the same time, the treatment resulted in an increase in combustion for both catalysts. This loss in selectivity on the Pd/SZ catalyst could be linked to the loss of sulfate or/and agglomeration of Pd. Under low O_2 partial pressure, Pd can undergo partial reduction and agglomerate into crystallite metallic Pd particle. A comparable study [5] on 0.3% Pd/H-ZSM-5 indicated that, when metallic Pd was exposed to $NO/CH_4/O_2$, Pd was oxidized and redispersed to Pd^{2+} ions. However, in this case with the zirconia-based catalysts, incorporating O_2 into the NO/CH_4 mixture after 1 h was not enough to completely redisperse the Pd upon re-oxidation, resulting in large PdO clusters that are not selective for NO reduction.

Furthermore, possible sulfate loss during the NO/CH_4 treatment may result in a lower concentration of anchoring sites for Pd^{2+} stabilization. A more dramatic effect was observed after the subsequent 1 h reduction in H_2. Pd/SZ lost 75% of its initial NO reduction activity while Pd/WZ retained its activity and selectivity. Methane combustion activities were slightly lower on both catalysts than before the H_2 treatment. Suppression after high temperature treatments in H_2 has been reported for CH_4 combustion on Pd catalysts [24]. The effect is possibly related to the removal of coordinatively unsaturated sites on PdO crystallites during reduction, which are responsible for the activation of CH_4 [25].

Our previous investigations showed that for every acidic supports, there is an optimum Pd content which exhibit maximum SCR activity and selectivity. The optimum Pd concentration varies with the saturation capacity of the support for Pd stabilization. Beyond this saturation Pd concentration, combustion begins to dominate [13]. We therefore performed the deac-
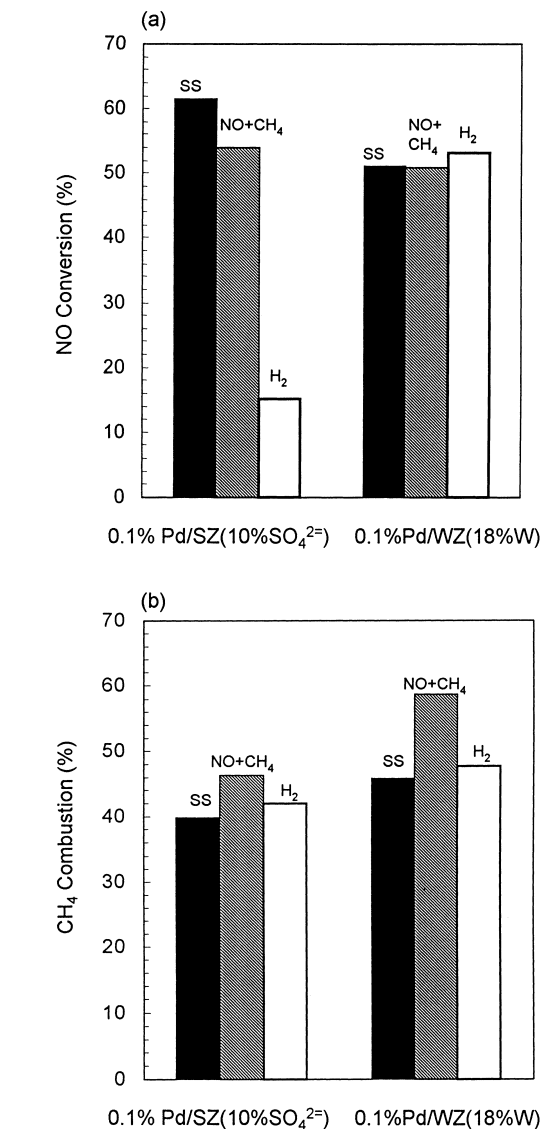

Fig. 2. Steady state NO conversion (a) and CH_4 combustion (b) on 0.1% Pd/10% SZ and on 0.1% Pd/WZ (12% W) catalysts after treatment in $CH_4 + NO$ (shaded bars) or treated in H_2 (open bars) for 1 h at 500°C, compared to the steady-state activities before the treatments (solid bars). Reaction conditions: 500°C, 40,000 GHSV, 3600 ppm NO, 7400 ppm CH_4, 1.9% O_2, balance He.

tivation studies on the best catalysts found for each series. The following experiments were conducted on H-MOR, SZ, and WZ with optimum Pd loadings of 0.2, 0.1 and 0.1 wt.%, respectively.

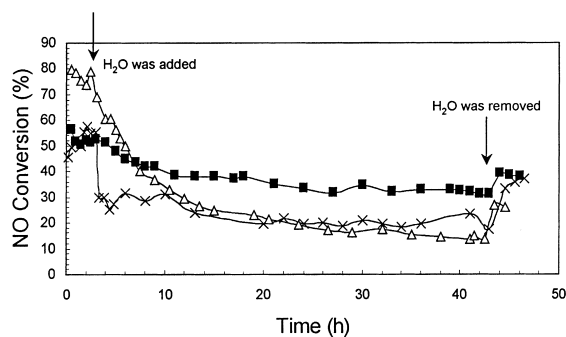To investigate the effects of H_2O and SO_2 poisoning, deactivation studies were conducted starting

Fig. 3. Effect of H_2O. Deactivation profiles on 0.2% Pd/H-MOR (triangles), 0.1% Pd/SZ (9.9 wt.% SO_4^{2-}) (squares), and 0.1% Pd/WZ (13.5 wt.% W) (crosses) in the presence of 10 vol.% H_2O. Reaction periods: 0–3 h clean SCR cycle, 3–43 h SCR cycle under 10% H_2O, 43–50 h clean SCR cycle. Reaction conditions: 0.21 g catalyst, 500°C, 3600 ppm NO, 7400 ppm CH_4, 1.9% O_2, balance He, with or without 10 vol.% H_2O in an overall flow of 72 cm^3/min.

Fig. 4. Effect of SO_2. Deactivation profiles on 0.2% Pd/H-MOR (triangles), 0.1% Pd/SZ (9.9 wt.% SO_4^{2-}) (squares), and 0.1% Pd/WZ (13.5 wt.% W) (crosses) in the presence of 75 ppm SO_2. Reaction periods: 0–3 h clean SCR cycle, 3–43 h SCR cycle under 75 ppm SO_2, 43–50 h clean SCR cycle. Reaction conditions were the same as those in Fig. 3, except under the 3–43 h poisoning period, 75 ppm SO_2 was added instead of H_2O.

with a 3 h period under dry/clean conditions followed by a 40 h period in the presence of 10% H_2O and 75 ppm SO_2, fed either separately or simultaneously. Each poisoning cycle was terminated by a dry/clean cycle to examine the activity recovery of each catalyst upon removal of impurities. Fig. 3 shows the NO conversion as a function of time-on-stream for 0.2% Pd/H-MOR, 0.1% Pd/SZ and 0.1% Pd/WZ catalysts, the data were taken with the same amount of catalysts, despite their difference in GHSV. It is seen that, although Pd/H-MOR was more active during the first dry cycle, addition of 10% of H_2O vapor suppressed NO reduction activity to a great extent. As water was added into the reactant stream during the second cycle (poisoned), the NO conversion drastically declined from 75 to 25% during the first 10 h, then continuously decreased to 15% at the end of the period. Under dry conditions, Pd/SZ exhibited a moderate NO conversion of about 50%. Addition of water suppressed the NO conversion to a lesser extent on this catalyst than on Pd/H-MOR. While the Pd/SZ catalyst retained 65% of its steady state "dry" activity at the end of the second poisoned cycle in H_2O, the Pd/H-MOR only retained 20%. On the other hand, the Pd/WZ sample under dry conditions had a NO reduction activity comparable to that of Pd/SZ, but it was more sensitive to H_2O than Pd/SZ. At the end of the poisoned cycle, Pd/WZ had the same activity as Pd/H-MOR. In the following dry cycle, after removal of H_2O, the NO conversions were
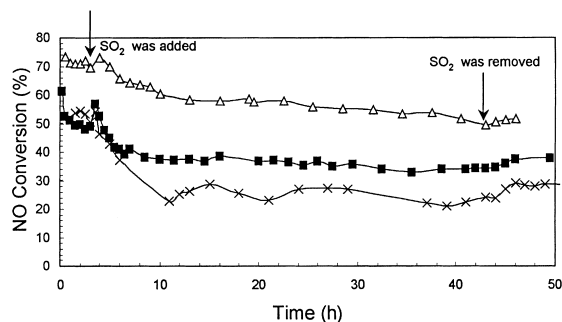
partially recovered for all the three samples, with the Pd/SZ recovering most of its initial activity.

Similar deactivation studies were conducted in the presence of SO_2 and H_2O/SO_2 mixture for all the three catalysts. The NO conversions obtained for these catalysts under SO_2 and H_2O/SO_2 are compared in Figs. 4 and 5, respectively. The deactivation profiles show that the inhibition is less pronounced with SO_2 than with H_2O vapor. Under SO_2, both Pd/H-MOR and Pd/SZ exhibited modest deactivation. The differ-
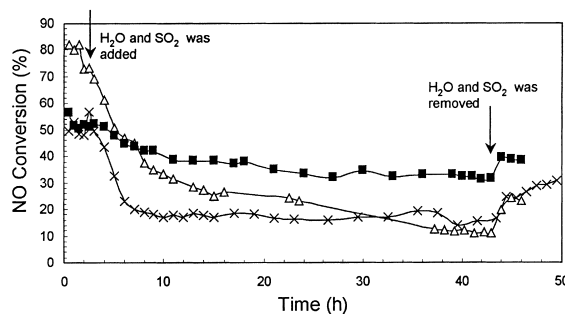

Fig. 5. Effect of H_2O and SO_2. Deactivation profiles on 0.2% Pd/H-MOR (triangles), 0.1% Pd/SZ (9.9 wt.% SO_4^{2-}) (squares), and 0.1% Pd/WZ (13.5 wt.% W) (crosses) in the presence of 10 vol.% H_2O and 75 ppm SO_2. Reaction periods: 0–3 h clean SCR cycle, 3–43 h SCR cycle under 10 vol.% H_2O and 75 ppm SO_2, 43–50 h clean SCR cycle. Reaction conditions were the same as those in Fig. 3, except under the 3–43 h poisoning period, 75 ppm SO_2 and 10 vol.% H_2O were simultaneously added.

Table 1
Steady-state catalytic activities of several Pd catalysts during clean and poisoned cycles[a]

Catalyst	No conversion (%) [CH$_4$ combustion (%)]			
	Impurity added	First cycle (clean)	Second cycle (poisoned)	Third cycle (clean)
0.2% Pd/H-MOR		70 [62]		
	SO$_2$		52 [35]	51 [37]
	H$_2$O		14 [5]	27 [18]
	H$_2$O + SO$_2$		11 [11]	24 [39]
0.1% Pd/SZ (9.9% SO$_4^{2-}$)		52 [20]		
	SO$_2$		34 [7]	38 [9]
	H$_2$O		32 [10]	48 [22]
	H$_2$O + SO$_2$		31 [1]	39 [14]
0.1% Pd/WZ (13.2% W)		55 [50]		
	SO$_2$		25 [15]	29 [23]
	H$_2$O		20 [10]	36 [50]
	H$_2$O + SO$_2$		17 [3]	31 [45]

[a] Reaction periods: 0–3 h first cycle (clean), 3–43 h second cycle (poisoned), 43–50 h third cycle (clean). Reaction conditions: 0.21 g catalyst, 500°C, 3600 ppm NO, 7400 ppm CH$_4$, 1.9% O$_2$, balance He, with or without 10 vol.% H$_2$O and/or 75 ppm SO$_2$ in an overall flow of 72 cm^3/min.

ence in activity between the two catalysts remains the same as under clean conditions. However, the Pd/WZ suffered a greater deactivation under SO$_2$, losing in the 40 h period almost 50% of the activity observed under clean conditions. Under the simultaneous addition of H$_2$O + SO$_2$, the advantage displayed by the zirconia-based catalysts over the zeolite-based catalyst under H$_2$O is once again evident. The deactivation patterns in the presence of H$_2$O + SO$_2$ are illustrated in Fig. 5. The deactivation trends for the three catalysts were very similar to those under H$_2$O, shown in Fig. 4. The incorporation of SO$_2$ in a wet stream, as compared to H$_2$O alone, does not seem to have any additional deactivation effects.

The steady state NO conversion and CH$_4$ combustion at the end of each cycle are summarized in Table 1. The zirconia-based catalysts show some similarities. For example, the suppressions in NO conversion were essentially the same under H$_2$O, SO$_2$ or H$_2$O + SO$_2$. By contrast, on the H-MOR, a most dramatic deactivation was observed in the presence of water. In addition, on the zirconia-based catalysts the CH$_4$ combustion was almost completely suppressed under H$_2$O + SO$_2$ although the NO conversion remained relatively high. Since most of the CH$_4$ converted was used for NO conversion a remarkable increase in selectivity was observed. By contrast, on the H-MOR there was only modest changes in selectivity under poisoning condi-

tions. Finally, upon removal of impurities (third cycle, clean), the CH$_4$ combustion on the two zirconia-based catalysts was regained, except under the poisoning of SO$_2$ alone. This behavior is again different from that observed on H-MOR. On this catalyst, CH$_4$ combustion was not regained after the removal of any of the impurities.

The promotion of Pd catalysts by the acidic supports can be, at least in part, attributed to the stabilization of Pd^{2+}. The formation of these Pd^{2+} ions can be probed by DRIFTS analysis of adsorbed NO. For example, it has been found that the NO reduction activity on Pd/H-ZSM-5, Pd/H-MOR, and Pd/H-Y catalysts correlates with the intensities of NO absorption bands at 1881 and 1836 cm^{-1} [26], which are ascribed to NO adsorption on Pd^{2+} ions. We have previously shown that SZ is able to stabilize the same Pd^{2+} species, giving the characteristic absorption bands in the same position. In contrast, on a non-selective Pd catalyst (0.3% Pd/SiO$_2$), NO adsorbed weakly and exhibited a lower frequency band at 1743 cm^{-1}. In this contribution we have compared DRIFT spectra of Pd/WZ, Pd/ZrO$_2$, WZ and ZrO$_2$ samples. As shown in Fig. 6, bare ZrO$_2$ or WZ alone do not absorb NO in the region of 1820–1890 cm^{-1}. The characteristic bands at 1868 and 1821 cm^{-1}, corresponding to the Pd ions, were only observed for the Pd/WZ catalysts, but not for the Pd/ZrO$_2$ sample, even though these samples
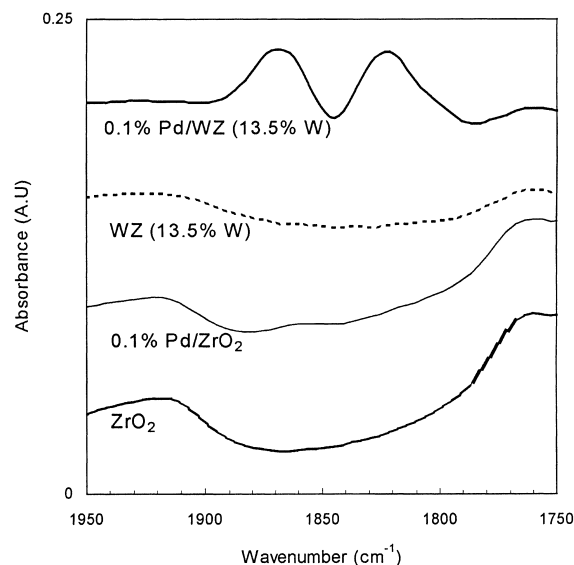
Fig. 6. DRIFT spectrum of NO adsorption on Pd/WZ (13.5 wt.% W), WZ (13.5 wt.% W), Pd/ZrO$_2$, and ZrO$_2$ after purging under He for 30 min, following adsorption of 5% NO/He at room temperature.

contained the same amount of Pd. This result indicates that, as opposed to non-acidic plain ZrO$_2$, the zirconia promoted with tungsten oxide exhibits the same Pd stabilization ability as the acidic zeolites and SZ.

4. Conclusions

Two non-zeolitic supports, sulfated zirconia (SZ) and tungstated zirconia (WZ), have shown to be effective in promoting the SCR activity of Pd by stabilizing Pd^{2+} ions, which are active for NO reduction but less active for methane combustion. These supports are more resistant than zeolites to deactivation by water and SO$_2$.

Acknowledgements

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