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Catalysis Today 62 (2000) 291–302

CATALYSIS TODAY

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Comparison between methane and propylene as reducing agents in the SCR of NO over Pd supported on tungstated zirconia

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Abstract

It is now well known that when Pd is supported on acidic supports, it becomes highly selective for the reduction of NO by methane in the presence of excess oxygen. It is also known that this promoting effect not only occurs with acidic zeolite supports, but also with acidic zirconia supports, such as sulfated zirconia (SZ) and tungstated zirconias (WZ). However, this promoting effect has not been investigated for the SCR with other hydrocarbons as reducing agents. In this contribution, we have investigated the behavior of a series of Pd/WZ catalysts and compared them using methane and propylene as reducing agents. The results show some important differences when the reducing agent is changed. For example, while with CH_4 the addition of W to the catalyst results in an increase in both NO and hydrocarbon conversion, with C_3H_6 it results in a decrease in activity. At the same time, while the presence of NO accelerates the activation of CH_4, it inhibits the activation of C_3H_6, moving its light-off to higher temperatures. Finally, an important difference between CH_4 and C_3H_6 as reducing agents is regarding the selectivity towards N_2 as opposed to N_2O. Using CH_4 resulted in much lower production of N_2O than using C_3H_6, over the entire temperature range investigated. © 2000 Published by Elsevier Science B.V.

Keywords: Reducing agents; Sulfated zirconias; Tungstated zirconias

1. Introduction

Emission of nitrogen oxides as byproduct of the high temperature combustion has been a major environmental concern. A large fraction of the vast research efforts conducted during the last decade in this area has focused on the catalytic reduction of NO using hydrocarbons in the presence of excess O_2, due to its applications in diesel and lean-burn engines [1,2]. One of the main challenges in this reaction is that, when excess O_2 is present, hydrocarbon combustion may dominate and inhibit the NO reduction. Studies in this area have been carried out on cation-exchanged zeolites [3] as well as on alumina-supported noble metals [4–6]. Among a large number of catalysts examined, noble metals catalysts can be able to promote high selectivity towards the reduction of NO at relatively low temperatures. Selectivity has been generally found to be a strong function of the amount of metal in the catalyst, as well as the support and the reducing agent used. For example, under the selective catalytic reduction (SCR) with CH_4, the performance of Pd catalysts could vary from almost inactive to active but unselective, passing through highly selective, depending on the metal loading as well as the support acidity [7,8]. High selectivities result from the ability of the catalyst to activate the hydrocarbon for reaction, but at the same time, suppressing the total combustion reaction to facilitate the NO reduction. It is normally found that the temperature for maxi-

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0920-5861/00/$ – see front matter © 2000 Published by Elsevier Science B.V.
PII: S0920-5861(00)00431-4

mum NO reduction activity follows the same trend observed in the light-off of the hydrocarbons. That is, it decreases with increasing the hydrocarbon order, e.g. C_3H_6 is activated at lower temperatures than CH_4. As proposed by Burch and Watling [9], when an olefin is used as a reducing agent instead of an alkane, the nature of the species present on the surface, as well as the oxidation state of the active metal may radically change. Therefore, different mechanisms may occur depending on the reducing agent used.

Another important consideration that needs to be made when comparing different reducing agents is in regards to the selectivity of NO conversion towards N_2 since the reduction of NO not only can produce N_2 but also N_2O, and this selectivity may depend on the reducing agent used. N_2O is a greenhouse gas, more than 300 times more potent than CO_2 and recent estimates indicate that N_2O now comprises about 7% of the gases that cause global warming. Cars and trucks produce nearly half of that N_2O and the N_2O emissions are increasing rapidly. The problem has worsened as catalytic converters improve. The changes that have eliminated more of the NO_x compounds (NO and NO_2) that cause smog, have conversely produced more nitrous oxide, N_2O. Nitrous oxide is not regulated because the Clean Air Act was written in 1970 to control smog, not global warming. No regulations exist yet to control gases that are believed to cause global warming. However, in the 1997 Kyoto meeting, the US and other committed countries agreed to lower emissions of greenhouse gases to 5% below the 1990 levels, over the next 10–15 years [10]. So, very soon N_2O may become regulated. Therefore, finding catalysts that produce minimum amounts of N_2O, that is, with a high selectivity towards $N_{2,}$ is an important research goal.

In our previous study, we have shown that Pd/ZrO_2 can become highly selective for CH_4-SCR when promoted by sulfate or tungstate-oxoanions [11]. These catalysts, were found to be more resistant to H_2O and SO_2 poisoning than zeolite-based catalysts in 40 h deactivation studies. In this contribution, we have examined the promotional effects of these catalysts, using either CH_4 or C_3H_6 as reducing agents, focusing not only on the activity and selectivity towards NO conversion, but also towards N_2 formation, rather than N_2O.

2. Experimental

Sulfated zirconia (SZ) and tungstated zirconia (WZ) supports were prepared by incipient wetness impregnation of ammonium sulfate (Mallinckrodt) and ammonium metatungstate (Aldrich) solution onto zirconium hydroxide ($Zr(OH)_4$, provided by MEI) following a drying period of 4 h at 110°C. H-Mordenite (H-Mor), with a SiO_2/Al_2O_3 ratio of 8, was obtained from UOP and was used as received. Prior to the addition of metals, all the supports were dried at 110°C and calcined. The SZ was calcined at 600°C under stagnant ambient air, while the H-Mor and WZ were calcined under flowing dry air (zero grade, Airgas). The H-Mor was calcined at 550°C for 3 h while WZ was calcined at 650°C for 90 min. In all cases, a heating ramp of 5°C/min was used. After calcination, the supports were stored at 110°C and then impregnated at incipient wetness with solutions of $Pd(NO_3)_2$ (Alfa Aesar) for the Pd catalysts or $[Pt(NH_3)_4](NO_3)_2$ (Aldrich) for the Pt catalyst. The incipient wetness points were found to be 0.37 and 0.89 cm^3/g for zirconia based materials and H-Mor, respectively. The metal loadings for the catalysts supported on zirconia-based materials was 0.1 wt.% (Pd or Pt), while for the catalyst supported on H-Mor, it was 0.2 wt.%. For comparison, two additional Pd samples were prepared. One of them was 0.1 wt.% Pd directly supported on bulk WO_3 (Aldrich, BET area 1 m^2/g). The second one was a 0.1 wt.% Pd/W-SiO_2. This sample was prepared by impregnating silica gel (Grade 923, W.R. Grace and Co.) with 13.2 wt.% W. Both samples were calcined and impregnated with Pd as described for the other catalysts.

Catalytic activity measurements were performed after heating in He with a ramp of 5°C/min. Activity measurements were then conducted using 0.21 g of catalyst and varying temperatures from 275 to 550°C at a space velocity of 40 000 h^{-1}. Reactant compositions were 3600 ppm NO, 7400 ppm CH_4 or 2400 ppm of C_3H_6, 1.5–1.9% O_2 in balance He. Depending on the hydrocarbon used, the amount of O_2 was altered such that 25% excess O_2 was always used in the feed. This excess was calculated based on the stoichiometry of the total combustion for each hydrocarbon. NO consumption and N_2O production were simultaneously monitored in a continuous mode using two chemiluminescence analyzers (models 42C and 46, from Thermal Environmental Inc.) that provide independent measurements of NO, NO_2, and N_2O concentrations. The consumptions of CH_4 and C_3H_6 were quantified with a FID detector.

Temperature programmed oxidation (TPO) of the spent catalysts was performed in a continuous flow of 2% O_2/He while the temperature was linearly increased. The reaction was conducted in a quartz fixed bed reactor and 50 mg of spent catalyst was supported on a bed of quartz wool. The oxidation of the carbon species deposited on the spent catalysts produced either CO or CO_2, which were then fully converted to CH_4 in a methanator device placed in front of a FID detector. Quantification of the CH_4 signal in FID was done by calibration with 50 μl pulses of pure CO_2 injected separately to the methanator. It is important to note that after the reaction period, the samples were purged in He at the reaction temperature and then cooled down under continuous He flow to avoid condensation of carbonaceous species and allow for the desorption of weakly held species.

Physical properties of the catalysts were determined on a Micromeritics ASAP 2010 N_2 adsorption apparatus, operating at liquid nitrogen temperature. CO_2 chemisorption measurements were conducted in a static volumetric adsorption Pyrex system, equipped with a high capacity, high vacuum station that provided vacuum on the order of 10^{-9} Torr. Prior to these adsorption measurements, the catalysts were pretreated in situ from room temperature to 400°C in zero grade air.

UV–VIS spectra were recorded in diffuse reflectance mode at room temperature in the range of 200–800 nm on a Shimadzu UV–VIS 2010 PC spectrophotometer, using $BaSO_4$ as a reference. Since the fundamental optical absorption energy for WO_x crystallites or amorphous WO_x species was mostly related to indirect electronic transitions ($\eta = 2$) [12], the absorption coefficient (α) is proportional to $(h\nu - E_0)^\eta/h\nu$ near the optical absorption edge energy E_0. Therefore, the E_0 values were determined by extrapolation of the linear portion of a plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ to the abscissa, at $(\alpha h\nu)^{1/2} = 0$ [13]. The position of the optical absorption edge energy is a function of the number of W sharing a common O in W–O–W structures, which is essentially the domain size of WO_x [14]. The DRIFTS absorption spectra of adsorbed NO were obtained using a Bio-Rad FTS-40 spectrometer, equipped with a MCT detector and a diffuse reflectance cell from Harrick Scientific, type HVC-DR2 with ZnSe windows. For each IR spectrum, taken at a resolution of 8 cm^{-1}, 128 scans were added. Samples were first pretreated in situ at 500°C and subsequently cooled, both under flowing He. They were then exposed to a 5% NO/He mixture at room temperature. The spectrum of each sample in pure He at room temperature was taken as a reference.

3. Results and discussion

3.1. Catalyst characterization

A series of WZ supports with nominal W-loadings ranging from 0 to 20.6% was prepared and characterized by N_2 adsorption/desorption, CO_2 chemisorption, and UV–VIS diffuse reflectance spectroscopy. XRD measurements (not shown here) indicated that, compared at the same oxidation temperature, addition of W resulted in a higher fraction of tetragonal ZrO_2. It is well known that addition of W delays the onset of ZrO_2 crystallization during thermal oxidation. By contrast, unpromoted zirconia, tends to sinter and to form the thermodynamically more stable monoclinic phase. Table 1 shows the structural characteristics of the supports after crystallization and oxidation at 650°C. Before crystallization, microporous $Zr(OH)_4$ had a BET area of 280 m^2/g. After crystallization under flowing dry air, the BET area varied with W concentration, with a maximum BET area of 121 m^2/g obtained at a nominal W-loading of 8.5%. The average pore diameter varied accordingly, but the pore volume for these catalysts remained essentially the same. To examine the fraction of ZrO_2 covered by WO_x, we conducted volumetric CO_2 chemisorption at room temperature. It is known that CO_2 adsorbs on the bare surface basic sites of the ZrO_2 but it does not adsorb on WO_3. Accordingly, from this measurement we were able to determine the fraction of the ZrO_2 surface that was covered by W. As shown in Table 1, this fraction increases linearly with the W content until about 13.2 wt.%. Above this loading, addition of W did not result in further reduction of the exposed ZrO_2 basic sites, which suggests that, at these loadings, the tungsten oxide species start forming multilayers. It is worth noting that at this loading (13.2 wt.%) the measured BET area was the highest in the series.

Table 1
Structural and chemical characteristics of the WZ supports used in the Pd/WZ series

W (wt.%)	BET area[a] (m^2/g)	Average pore diameter[a] (Å)	Pore volume[a] (cm^3/g)	Fraction of ZrO_2 covered by W[b]	Absorption edge energy[c] (eV)
0.00	108	74	0.201	0.000	–
3.78	113	71	0.200	0.143	3.74
5.87	116	70	0.202	0.279	3.47
8.50	121	67	0.202	0.451	3.33
13.22	113	72	0.202	0.702	3.26
17.35	–	–	–	0.690	3.25
20.56	106	75	0.203	0.757	3.20
WO_3 crystallite (reference)	–	–	–	–	2.40
Na_2WO_4 (reference)	–	–	–	–	4.34

[a] Determined by nitrogen adsorption/desorption measurements.
[b] Determined by CO_2 chemisorption measurements.
[c] Determined by UV–VIS spectroscopy.

The size of the WO_x domains can be probed by UV–VIS spectroscopy, since transition metal-oxides have optical absorption edges, which are within this region in the electromagnetic spectrum. Fig. 1 shows the absorption spectra for the catalyst series with varying W-loading. It is observed that the absorption curves lie between those of $NaWO_3$ and bulk WO_3. These two standard references have been previously used to represent isolated W ions, tetrahedrally coordinated to oxygen, and six-coordinated W in three-dimensional crystals, respectively [15]. Therefore, it can be concluded that in all the samples of this series, tungsten oxide species are present in small domains. These species increase in size as the W-loading increases. However, even at the highest W-loading (20.5 wt.%) large crystalline WO_3 clusters were not formed in significant quantities. To show this trend more clearly, we have included in Table 1 the E_0 values derived from the UV absorption spectra as described above. The data show that the E_0 values decreased from 3.74 to 3.20 eV as the W-loading increased. They are smaller than the value corresponding to isolated W ions (4.34 eV) but above the 2.40 eV value of bulk WO_3. The lack of a low-energy band corresponding to bulk WO_3 indicates that after the formation of a monolayer at around 13 wt.% W, the growth of three-dimensional structures is, at least up to loadings of 20.5 wt.% W, relatively slow. Other authors have observed the appearance of WO_3 on samples with similar W contents to those used in this work, but at higher calcination temperatures (800°C) than that used in this work (650°C). When they conducted their calcination at 700°C, no WO_3 species were detected, in agreement with our observations.

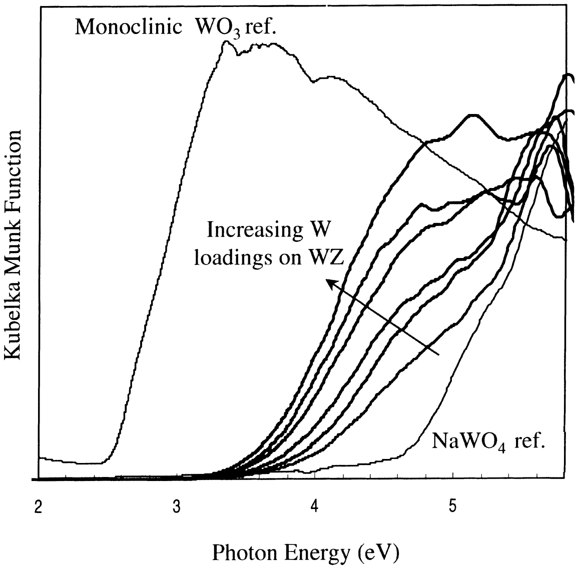

Fig. 1. Diffuse reflectance UV–VIS absorption spectra of a series of WO_x/ZrO_2 support samples (WZ) with increasing W-loading: 3.8, 5.9, 8.5, 13.2, 17.3, 20.5% W.

3.2. NO reduction with methane over Pd/WZ Series

It is now well established that when CH_4 is used as reducing agent for SCR, Pd catalysts can become highly selective when the typically high combustion activity of Pd is suppressed [8,16]. Several studies have shown that this promotional effect can only be obtained when small amounts of Pd are loaded on acidic supports [17] and that the presence of Brønsted acid sites is required to stabilized Pd in the form of isolated Pd^{2+} ions [18,19]. These Pd^{2+} ions, unlike PdO clusters, exhibit high selectivity towards NO conversion. Our most recent studies have demonstrated that not only acidic zeolites, but also SZ supports are able to stabilize Pd^{2+} ions [20]. The NO reduction activity on a series of 0.1% Pd/SZ catalysts with varying sulfate loadings increased with the nominal sulfate concentrations on the supports. Otherwise, without the presence of surface sulfate, even low loadings of Pd are enough to form PdO clusters that are not selective for the SCR reaction. We have now extended our study to supports prepared with zirconia promoted with tungsten-oxoanions. The so-called WZ is a material with high thermal stability [21], which exhibits significant activity for acid-catalyzed reactions [22].

As done in previous contributions, we usually report the NO conversions together with the CH_4 combustion that accompanies the NO reduction process. That is, from the total CH_4 conversion, we subtract the fraction of CH_4 that is used in the reduction of NO and we call this difference the "CH_4 combustion under SCR" to distinguish it from the "direct CH_4 combustion" that occurs in the absence of NO. The calculation of the amount of hydrocarbon that is used in the reduction of NO is simpler when CH_4 is the reductant, because the production of N_2O is negligible, as shown below.

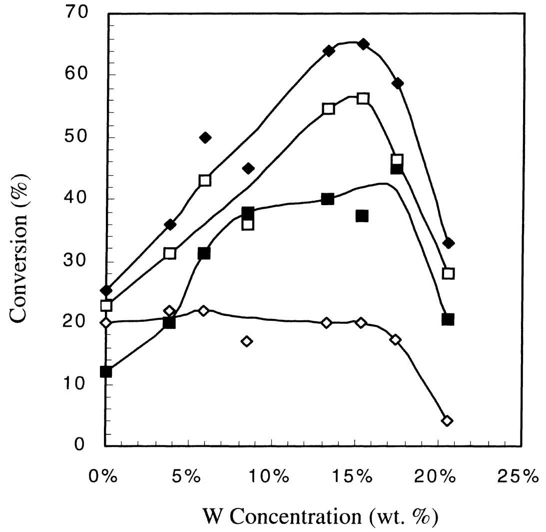

Fig. 2. Catalytic activity as a function of W-loading on a series of 0.1 wt.% $Pd/WO_x/ZrO_2$ catalysts. NO conversion (solid squares), CH_4 conversion (solid diamonds), calculated CH_4 combustion under SCR (open squares) and direct CH_4 combustion under CH_4+O_2 (open diamonds). Reaction conditions: 500°C, 0.21 g catalyst, 40 000 GHSV. Feed composition: 3600 ppm NO; 7400 ppm CH_4; 1.9% O_2; balance He, in an overall flow of 72 cm^3/min.

Accordingly, Fig. 2 shows the NO conversion, the total CH_4 conversion, the CH_4 combustion under SCR, and the direct CH_4 combustion (i.e. $CH_4 + O_2$ in the absence of NO) for a series of Pd/WZ catalysts with increasing W-loadings at a GHSV of 40 000 h^{-1}. Clear trends can be observed in this figure. It was found that the addition of W enhanced the NO reduction activity up to about 13–17 wt.% W, reaching a significant NO conversion (about 40%) at a high GHSV. It is important to note, that these catalysts were also active and selective for SCR in the presence of impurities. Table 2 summarizes the NO and CH_4 conversions obtained on the 0.1% Pd/(13.2 wt.% W)WZ in the presence of 10% H_2O and/or 75 ppm SO_2 at the end of a 40 h reaction period. It is observed that, when H_2O is present, the Pd/WZ catalyst compares very favorably with a typical Pd/H-Mor catalyst tested under the same conditions. Note that in terms of bed volume the GHSV of the WZ catalyst is higher, while per total catalyst weight they are the same, but with the WZ catalyst using less Pd.

The observed behavior is similar to that of the Pd/SZ catalysts. It appears that in both series the

Table 2
Catalytic activities of Pd/H-Mor and Pd/WZ under clean and poisoned conditions[a]

	NO conversion (%) (CH_4 combustion (%))	
	Catalyst	
	0.2% Pd/ H-Mor	0.1% Pd/ (13.2% WZ)
Without impurities	70 (62)	55 (50)
After 40 h reaction under	–	–
75 ppm SO_2	52 (35)	25 (15)
10% H_2O	14 (5)	20 (10)
10% H_2O + 75 ppm SO_2	11 (11)	17 (3)

[a] 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 and/or 75 ppm SO_2 in an overall flow of 72 cm^3/mm. This corresponds to 10 000 and 40 000 GHSV for H-Mor and WZ samples, respectively.

promotional effects of W (or sulfate) at low concentrations may be related to the presence of Brønsted acid sites [23], which can stabilize the selective Pd^{2+} ions. However, there are some important differences that we must point out. For example, the CH_4 combustion under SCR shows a pattern almost identical to that of NO conversion, in contrast with the behavior on Pd/SZ, which showed that the increase in sulfate concentration resulted in promotion of selectivity by suppressing the undesired CH_4 combustion [20]. Here, it appears that the addition of W promoted both NO reduction and CH_4 combustion under SCR conditions. It is therefore clear that W not only promotes the reduction of NO, but also the activation of CH_4. As also shown in Fig. 2, this promotion was not observed in the absence of NO, which might indicate that the activation of CH_4 proceeds via NO or NO_2 species.

As shown in the figure, the direct CH_4 combustion without NO over the unpromoted Pd/ZrO_2 catalyst was about the same as that over the W-containing catalysts up to a W-loading of about 16 wt.%. Contrasting with this trend, on Pd/SZ catalysts the CH_4 combustion in the presence of NO was lower than in its absence at low sulfate concentrations, but higher at high sulfate concentrations. Fig. 3 makes a comparison of the direct CH_4 combustion without NO in the feed and the CH_4 combustion under SCR for a series of Pd catalysts: an unpromoted Pd/ZrO_2, two promoted zirconia catalysts (Pd/SZ and Pd/WZ), and two reference samples ($Pd/W\text{-}SiO_2$ and Pd/WO_3). The sample supported on SiO_2 had the same W-loading as the most active Pd/WZ catalyst, which allows to determine whether the promotion observed on WZ-supported catalysts is due to simply the presence of W or to unique species generated on the zirconia. In fact, this sample showed moderate methane conversion under SCR and very low NO conversion, indicating that the presence of W alone is not enough to promote the SCR activity. Similarly, when Pd was supported on bulk WO_3, it was practically inactive. Of course, the dispersion of W on these reference samples is very different from that on the WZ series. Therefore, this comparison may not be entirely valid. However, it shows two important results. First, the presence of W alone cannot account for the observed promoting effects. It is the combination of Pd, W, and zirconia that makes the effective catalysts. Second, even though on a low surface-area support the Pd dispersion may be low and high combustion activity should be expected [24], the combustion was very low on these catalysts.

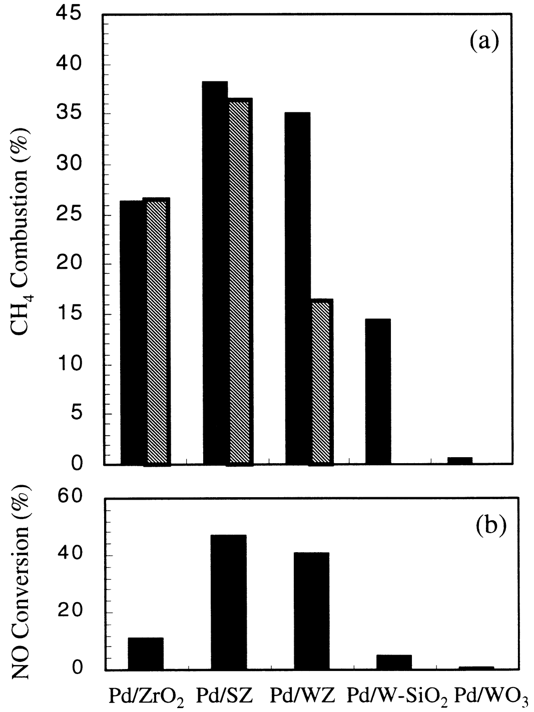

Fig. 3. (a) CH_4 combustion under SCR (solid bars) and direct CH_4 combustion (shaded bars) over several 0.1 wt.% Pd catalysts. The $Pd/WO_x/ZrO_2$ and the $Pd/WO_x/SiO_2$ catalysts contained 13.2 wt.% W, the Pd/SZ had 9.9 wt.% SO_4^{2-}. All catalyst had 0.1 wt.% Pd. (b) NO conversion under SCR for the same samples. Reaction conditions and amount of catalyst for SCR were the same as those in Fig. 1. $Pd/WO_x/SiO_2$ has different density, so the GHSV is different when keeping the same amount of sample and the same flow; for direct combustion ($CH_4 + O_2$): 7500 ppm CH_4, 1.9% O_2, balance He, same amount of catalyst.

Comparing the unpromoted Pd/ZrO_2 and the Pd/SZ, the differences in methane combustion with and without NO were relatively small. However, on the Pd/WZ the direct activation of CH_4 in the absence of NO was found to be greatly inhibited. These results suggest that on the Pd/WZ most of the Pd is stabilized in the highly dispersed form, which is inactive for direct CH_4 combustion and can only activate CH_4 through an NO-intermediate. The stabilization of highly dispersed Pd species is certainly possible in a zeolite [25], but it is not immediately obvious how can also occur on a support such as tungstated zirconia. In previous work, we have used DRIFTS of adsorbed NO to identify the presence of these species [20]. On low-loading Pd catalysts supported on H-ZSM-5 and H-Mor zeolites clear bands were observed at 1881 and 1836 cm^{-1}. These bands have been previously reported by Gelin et al. [26], who ascribed them to isolated Pd^{2+} ions. Interestingly, we observed the same bands on Pd/SZ catalysts [20]. In the present work on the Pd/WZ series, similar bands were observed at 1868 and 1821 cm^{-1}. The DRIFTS spectra for the current Pd/WZ series with the same Pd concentration but varying the amount of W are shown in Fig. 4, along with spectra of Pd/ZrO_2 and bare WO_x/ZrO_2 as references. The position and intensities of the bands at 1868 and 1821 cm^{-1} are similar for all the Pd/WZ catalysts, which could then be taken as an indication of the presence of Pd^{2+} species on all the samples of the series. A slight shift towards higher frequencies is observed when the W-loading becomes higher than that required to form a monolayer (13.2 wt.%). In contrast, the DRIFT spectrum of the Pd supported on unpromoted ZrO_2 did not show these absorption bands, but only that corresponding to PdO clusters around 1760 cm^{-1}. Thus, we have concluded that the presence of W is necessary to promote the formation of the selective, highly dispersed Pd species. The Brønsted acidity associated with tungsten oxide species of intermediate domain size [15] may be responsible for the observed stabilization of highly dispersed Pd ions. However, the presence of these Pd^{2+} ions alone does not guarantee the activity, as a wide range of activity and selectivity were observed on these samples. It is possible that W not only stabilizes Pd in a highly dispersed state, but it may also have an additional role in the reaction, such as directly providing active sites.

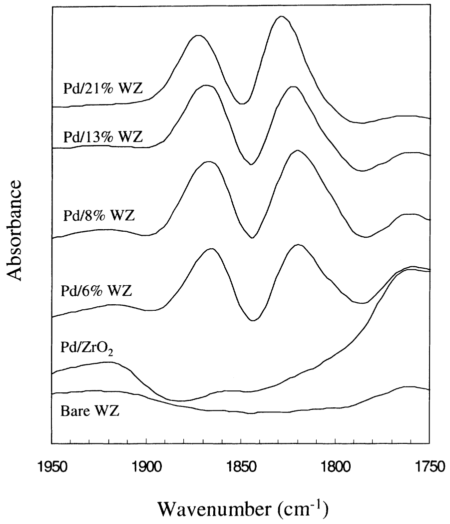

Fig. 4. Infrared spectra of NO adsorbed at room temperature on a series of 0.1% $Pd/WO_x/ZrO_2$ catalysts with various W-loadings (wt.% W indicated in each spectrum). Spectra for two additional samples, bare WO_x/ZrO_2 (noted WZ) and 0.1% Pd/ZrO_2 are included for reference. The spectra were taken after purging in He for 30 min following adsorption of 5% NO/He at room temperature.

The drop in activity at high W-loadings observed in Fig. 2 deserves further inspection. The activity suppression was not only observed on NO and CH_4 conversion under SCR, but also in the direct CH_4+O_2 reaction, in the absence of NO. One possible explanation could be the formation of bulk crystalline WO_3 at high W-loadings [27]. Large WO_3 aggregates might block pores, reducing the accessibility of reactants. However, as mentioned above, UV–VIS spectroscopy does not provide evidence for the formation of large WO_3 aggregates, while the physical adsorption measurements only showed minimal losses in BET area and pore volume on the high W-loading samples as compared to those on the low W-loading samples. Another possibility is that Pd becomes less accessible to the gas phase at high W-loadings. Pd and W oxides have been found to interact at high temperatures leading to the formation of solid solutions [28]. It is possible that for the interaction to occur a three-dimensional structure of tungsten oxide is necessary and that can only occur at high W-loading. With the small Pd loadings of these catalysts, even a small degree of interaction might result in a significant activity drop.

3.3. Comparison of methane and propylene as reducing agents

We have investigated the use of CH_4 and C_3H_6 as reducing agents on several Pd catalysts. NO conversions under SCR with CH_4 and C_3H_6 at different temperatures are shown in Fig. 5a and b, respectively. For all the WZ series a space velocity (GHSV) of 40 000 h^{-1} was used, due to the difference in density, the space velocity that results for the Pd/H-Mor catalyst when keeping the same catalyst weight is significantly lower, 10 000 h^{-1}. Several points can be immediately noted

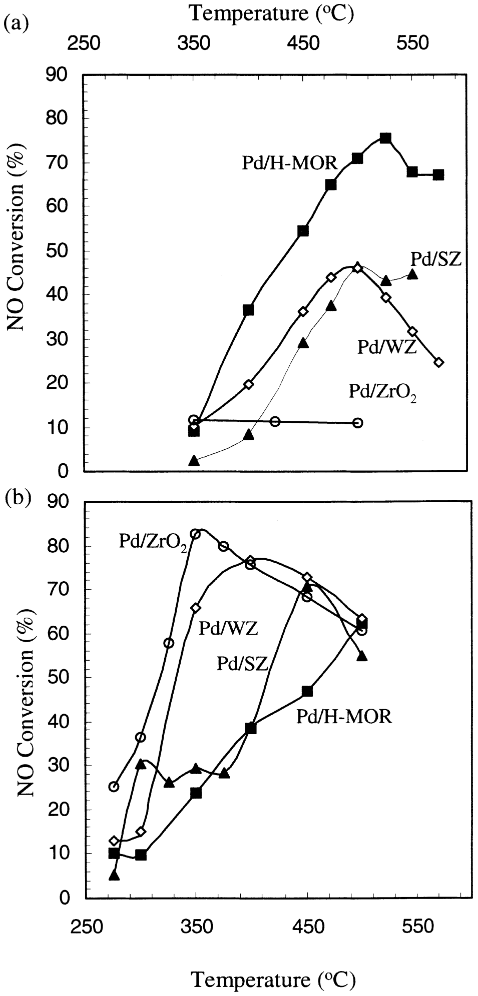

Fig. 5. NO conversion as a function of temperature over several 0.1 wt.% Pd based catalysts under SCR with CH_4 (a), and with C_3H_6 (b). The Pd loading on Pd/H-Mor was 0.2 wt.% Pd, for the rest it was 0.1 wt.% Pd. Reaction conditions: 0.21 g catalyst, 3600 ppm NO, 7400 ppm CH_4 or 2400 ppm C_3H_6; 0 and 1.5–1.9% O_2, balance He, in an overall flow of 72 cm^3/min. Depending on the hydrocarbon used, the amount of O_2 was varied such that reaction proceeded in 25% excess O_2, calculated based on total hydrocarbon combustion. The GHSV for Pd/H-Mor and zirconia based catalysts were 10 000 and 40 000 h^{-1}, respectively.

in these data. First, it is clear that when using CH_4 as the reducing agent, the presence of acid sites is essential to have NO reduction activity. Pd supported on unpromoted ZrO_2 is not selective, but when supported on acidic supports, it exhibits high selectivity. It can be observed that over the temperature range investigated (i.e. 350–550°C), Pd/H-Mor was the most active catalyst for NO reduction, followed by Pd/SZ and Pd/WZ. However, this advantage is only observed under clean reaction conditions. In previous work [20,11], we have shown that although catalysts supported on acidic zeolites, such as H-ZSM-5 and H-Mor are highly selective under clean conditions, their activity is severely suppressed in the presence of H_2O. By contrast, catalysts supported on acid-promoted zirconia display high resistance to H_2O and SO_2 poisoning.

The second point that is immediately obvious is that the trend obtained with C_3H_6 (Fig. 5b) as a reducing agent was the opposite to that obtained with CH_4 (Fig. 5a). That is, with C_3H_6, the unpromoted Pd/ZrO_2 exhibited higher activity than those in which Pd was supported on the acidic materials. Therefore, it is clear that the important characteristics that result in an effective SCR catalyst using CH_4 as a reducing agent do not apply when using C_3H_6. That is, the stabilization of Pd^{2+} species, necessary when using CH_4, does not seem to be important when using C_3H_6.

Fig. 6 compares the light-off curves for the total conversion of CH_4 and C_3H_6 under SCR for the same runs of Fig. 5. As expected, C_3H_6 is activated at much

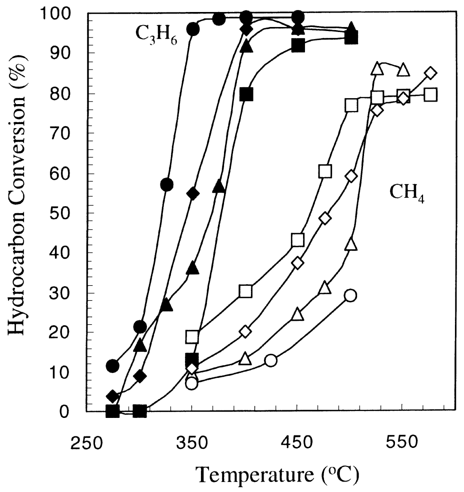

Fig. 6. CH_4 and C_3H_6 conversions during the SCR reaction, corresponding to the NO conversion data shown in Fig. 5a and b, respectively. Pd/ZrO_2 (circles), Pd/WZ, (13.2 wt.% W) (diamonds), Pd/SZ (9.9 wt.% SO_4^{2-}) (triangles), Pd/H-Mor (squares). The Pd loading in Pd/H-Mor was 0.2 wt.% Pd, in the rest it was 0.1 wt.% Pd. Reaction conditions were those of Fig. 5.

lower temperatures than CH_4. Here again, the greatest difference is observed on Pd/ZrO_2, which shows the highest hydrocarbon conversion with C_3H_6 but the lowest with CH_4.

Most studies in the literature dealing with SCR with hydrocarbons have focused on the activity of supported Pt catalysts. We have compared the SCR activity of Pd/ZrO_2 to a typical Pt/ZrO_2 catalyst with the same amount of metal loading as a function of temperature, using C_3H_6 as a reducing agent. As shown in Fig. 7, the Pd/ZrO_2 catalyst compared very favorably with the Pt catalyst, being significantly more active at lower temperatures, with a light-off occurring at almost 40°C lower.

The overall NO conversion reported above is the total amount of NO_x converted to both N_2 and N_2O. Table 3 makes a comparison of the N_2/N_2O selectivity. In this table, this selectivity is reported as the fraction of the total NO converted that produced N_2O rather than N_2. A remarkable difference in selectivity is observed depending on the reducing agent used. When using CH_4 the selectivity towards undesirable N_2O was very low, particularly for the catalyst supported on the acidic materials. On the other hand, under SCR with C_3H_6, the production of N_2O was significantly higher at both low and high temperatures.

Table 3
N_2/N_2O selectivity over several Pd catalysts under SCR with methane or with propylene

Catalyst	Percentage of total NO converted that produced N_2O			
	SCR with C_3H_6		SCR with CH_4	
	350°C	500°C	350°C	500°C
0.1% Pd/ZrO_2	28	21	4	13
0.1% Pd/13.2% WZ	22	18	0	2.2
0.2% Pd/H-Mor	7	17	31	0
0.1% Pt/ZrO_2	26	11	0	0

3.4. Temperature dependence of the SCR activity of the Pd/WZ series using C_3H_6 as a reducing agent

We have examined the temperature dependence of the activity of Pd/WZ catalysts containing the same Pd loading (0.1 wt.%) but increasing W concentrations. The NO conversion as a function of temperature is illustrated in Fig. 8. It is observed that, increasing the W concentration in the catalyst resulted in a shift in the light-off curves for NO conversion to higher temperatures, showing that the addition of W resulted in an inhibition rather than a promotion of activity. As shown in Fig. 9, this inhibition was also observed in the conversion of C_3H_6 under NO + C_3H_6 + O_2. At

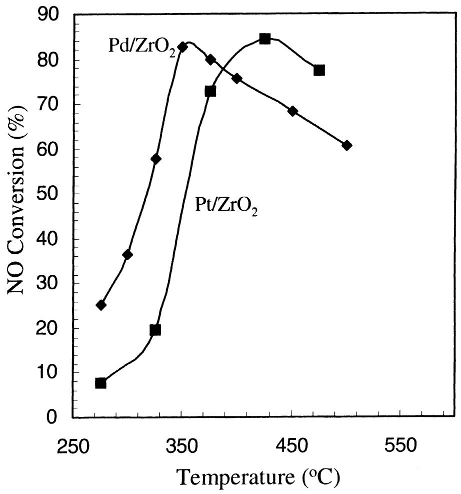

Fig. 7. Comparison of NO conversion on 0.1 wt.% Pd/ZrO_2 and 0.1 wt.% Pt/ZrO_2 catalysts under C_3H_6 SCR. Reaction conditions: 40 000 GHSV, 0.21 g catalyst under 3600 ppm NO, 2400 ppm C_3H_6, 1.5% O_2, balance He.

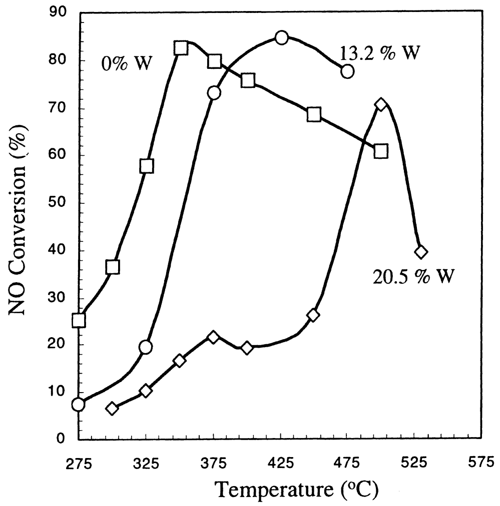

Fig. 8. NO conversion over 0.1 wt.% Pd/WZ catalysts containing different amounts of W under C_3H_6 SCR. Reaction conditions were the same as those in Fig. 7.

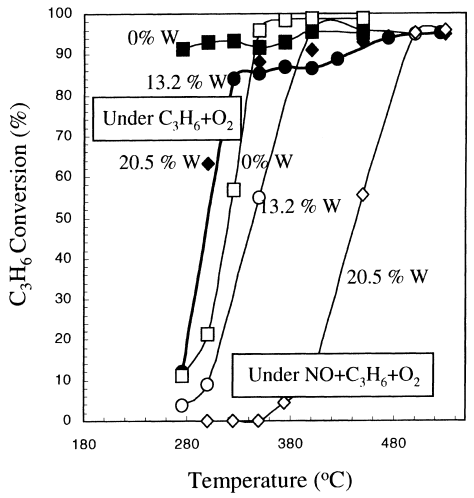

Fig. 9. Total C_3H_6 conversion under SCR with C_3H_6 (open symbols) and direct combustion of C_3H_6 (full symbols) over several 0.1 wt.% Pd/WZ catalysts, containing different amounts of W. Reaction conditions were the same as those in Fig. 7 for the SCR. In the direct C_3H_6 combustion NO was removed from the feed, while keeping the other concentrations unchanged.

the same time, Fig. 9 illustrates the light-off curves on the different catalysts during the direct combustion of C_3H_6 in the absence of NO. Unpromoted Pd/ZrO_2 was much more active for the C_3H_6 combustion than the W-promoted samples. It is interesting to note that while the samples with 13.2 and 20.5 wt.% W exhibited almost the same light-off curve in the absence of NO, the one with higher W content was much less active under SCR conditions.

From an analysis of the SCR rate dependence on oxygen concentration, Burch et al. [9] have proposed that, when using C_3H_6 as a reducing agent for the SCR on Pt catalysts, the Pt surface should be free of oxygen, consistent with the observed first order dependence on oxygen partial pressure. By contrast, when C_3H_6 was replaced by propane, the reaction order with respect to oxygen became zero, indicating that under these reaction conditions, the surface was covered by oxygen. These ideas may very well explain the differences between the results with C_3H_6 and with CH_4 that we report in the present contribution.

In the first place, we have observed that the presence of W on the catalysts has a different effect depending on the reducing agent being used. While W promotes the SCR activity of the catalysts when the reducing agent is CH_4, it actually inhibits the activity with C_3H_6. The promoting effect of the support when using CH_4 as a reducing agent has already been explained in previous papers [16]. XANES results [17] have shown that at the high temperatures required to activate CH_4 (e.g. 500°C), and in the presence of excess O_2, Pd is oxidized. The stabilization of Pd^{2+} ions on WZ, SZ, and all the acidic zeolites has been demonstrated by EXAFS and FTIR [17,20,11]. The promoting effect of acid supports is therefore mostly due to the inhibition of the competing direct CH_4 combustion by stabilization of Pd^{2+} ions, minimizing the presence of the unselective PdO clusters. The contrasting effects of W when using C_3H_6 as a reducing agent may be explained considering the higher reactivity of this reducing agent. Under these conditions, Pd may not be in the oxidized state, but rather as a metal, partially covered by carbonaceous species. Therefore, the presence of acidity on the surface is not longer beneficial, but rather detrimental. Propylene can easily form carbonaceous deposits, which may not only reduce the surface of the metal as proposed by Burch, but also inhibit the activity of the catalyst. Therefore, if the presence of W further increases the rate of carbon deposition on the catalyst, it will result in the observed SCR inhibition.

To test this possibility we have conducted TPO of the carbonaceous deposits left on the catalysts after 1 h SCR reaction. TPO profiles were obtained after reaction at 350°C using C_3H_6 as a reducing agent and 500°C using CH_4. These two temperatures were selected as the conditions for which the catalysts show the optimum performance with each reductant. Two catalysts with the same Pd loading (0.1 wt.% Pd) but varying W concentration (13.2 wt.% W and 20.5 wt.% W) were compared. As predicted above and shown in Fig. 10, the SCR reaction at 350°C and using C_3H_6 resulted in a much larger extent of carbon deposition than that at 500°C using CH_4. Quantification of the amount of carbon deposited in each run indicated about 0.2 wt.% C for C_3H_6 and about 0.03 wt.% C for CH_4. The W concentration did not have a great effect on the amount of carbon deposited. However, it had an important effect on the nature of the carbonaceous deposits. It was observed that as the W content on the catalysts increased the position of the TPO peak shifted to higher temperatures. It is interesting to compare the amount of carbon that can be removed at

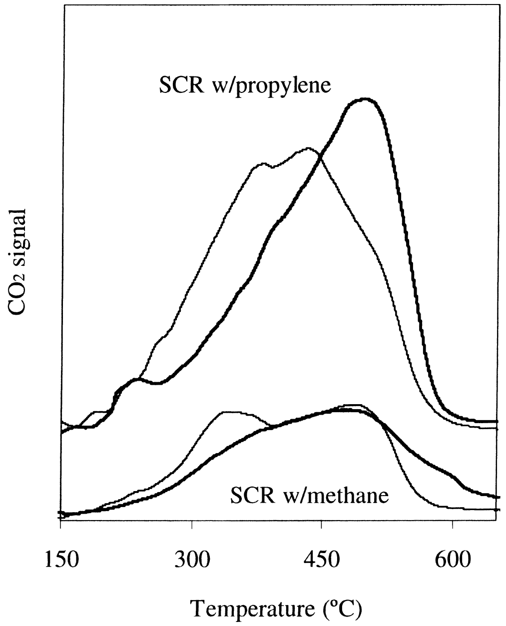

Fig. 10. TPO of carbonaceous deposits after 1 h SCR reaction runs. Top lines correspond to SCR runs with C_3H_6, bottom lines correspond to SCR runs with CH_4. Heavy lines: 0.1 wt.% Pd/WZ (20.5 wt.% W); Single lines: 0.1 wt.% Pd/WZ (13.2 wt.% W).

temperatures higher than that at which the SCR reaction was conducted. If the deposition and removal of carbonaceous species is a dynamic process under reaction conditions, the fraction that can only be oxidized at temperatures above the reaction temperature, may be severely deactivating. As seen in Fig. 10, greater amounts of this type of carbon were observed on the catalyst with higher W content. This difference was similar when using either C_3H_6 or CH_4 as reductant, operating at either 350 or 500°C, respectively. The inability to remove this type of carbon under reaction conditions might contribute to the observed decrease in SCR activity of the catalysts with high W-loadings.

Finally, another important difference observed on the Pd/WZ catalysts is the contrasting effect of NO in the activation of the hydrocarbon. By comparing Figs. 2 and 9, it can be concluded that while NO promotes the activation of CH_4 under SCR conditions, it actually inhibits the activation of C_3H_6. Since C_3H_6 can be easily activated, the presence of NO, may interfere by competing for the adsorption sites responsible for C_3H_6 activation. On the other hand, since the activation of CH_4 is more difficult, it is possible that adsorbed NO, or most probably, adsorbed NO_2, can in fact promote the CH_4 activation.

4. Conclusions

The selective catalytic reduction of NO by hydrocarbons on Pd catalysts displays different trends depending on the type of reducing agent employed. The following trends have been observed.

1. When CH_4 is used, the addition of W to the support results in an increased activity for both NO reduction and hydrocarbon conversion. Only at W contents exceeding about 15 wt.%, does the activity decreases.
2. Similarly, when CH_4 is used, the Pd/ZrO_2 catalyst in the absence of W or S is almost inactive for NO reduction and very unselective.
3. By contrast, when C_3H_6 is used, the unpromoted Pd/ZrO_2 catalyst is the most active for SCR, and the presence of promoters or acidity on the support only results in activity suppression.
4. Pd/ZrO_2 appears as a promising SCR catalyst when C_3H_6 is used as a reducing agent, exhibiting higher activity than a Pt/ZrO_2 catalyst, which contained the same amount of metal (by weight).
5. An advantage in favor of CH_4 over C_3H_6 as a reducing agent is the much lower production of the undesired SCR by-product N_2O. For all the Pd catalysts, the use of CH_4 resulted in higher N_2 selectivities over the whole temperature range investigated.

Acknowledgements

This work has been supported by the National Science Foundation by a grant number CTS-9726465 and by INT-9803052 for a collaborative agreement between the US and Argentina.

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