Selective NO_x reduction during the $H_2 + NO + O_2$ reaction under oxygen-rich conditions over $Pd/V_2O_5/Al_2O_3$: evidence for *in situ* ammonia generation

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Under oxygen-rich conditions in $H_2 + NO + O_2$ mixtures, $Pd/V_2O_5/Al_2O_3$ catalysts are active and highly selective (~80%) for NO_x reduction to N_2. *In situ* DRIFT spectroscopy and reactor data show that the system operates via formation of NH_x species on the highly dispersed V_2O_5 component. Both NH_3 and NH_4^+ are formed, with the latter dominant. The role of the palladium component is also discussed.

KEY WORDS: NO; palladium; H_2; N_2O; lean burn; Al_2O_3; V_2O_5; FTIR; DRIFTS.

1. Introduction

Catalytic reduction of the nitrogen oxides (NO, NO_2) produced by lean burn gasoline and diesel engines is problematic due to the very high oxygen concentrations present in the exhaust streams. This makes effective utilization of any available reductants (HC, CO, H_2) for NO_x removal extremely difficult, as these species are consumed preferentially by reaction with O_2 [1,2]. The control of NO_x emissions from stationary power sources and various chemical plants is also environmentally important. For these applications, the NH_3 SCR process [3,4], employing V_2O_5/TiO_2-based catalysts, is currently the most widely used option for NO_x abatement. Ammonia is employed as it displays very high selectivity toward NO_x even under these highly oxygen-rich conditions. Although very effective, the requirement for a separate NH_3 reservoir and injection system disfavors the use of this technology for transport applications. Safer alternatives such as urea, the decomposition of which can be used to make ammonia, have therefore been extensively studied [5–7]. Strategies for onboard NH_3 formation have also been discussed [8].

Recently, we showed that Pd/TiO_2 catalysts can generate NH_3 *in situ* when fed with $H_2 + NO + O_2$ under oxygen-rich conditions, resulting in very high NO_x conversions (70–80%) being attained [9]. The high activity of Pd/TiO_2 under these conditions was first reported by Ueda *et. al.* [10,11]. Two separate pathways for NO_x reduction were observed, operating at different temperatures. Employing *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) [9], we were able to assign the low-temperature process at ~120 °C (the temperature region where H_2 conversion approaches 100%) to dissociation and reaction of NO on reduced (Pd^0) metal sites. In contrast, the high-temperature mechanism at ~240 °C was shown to operate via the formation and subsequent reaction of NH_3. A similar mechanism was recently proposed by Burch and Coleman to account for the promoting influence of MoO_3 in $Pt/MoO_3/Al_2O_3$ catalysts during the $H_2/NO/O_2$ reaction under oxygen-rich conditions [12].

In this paper, we report on the $H_2 + NO + O_2$ reaction over a $Pd/V_2O_5/Al_2O_3$ catalyst. This system has been studied by a combination of reactor measurements and DRIFT spectroscopy. It is shown that at temperatures above 200 °C, the Pd/V_2O_5-based system performs in a similar manner to that reported previously for Pd/TiO_2-generating NH_x species *in situ*, which subsequently result in very high NO_x conversions being attained. Indeed, the V_2O_5-based catalyst was found to deliver significantly improved NO_x conversion (~90%) compared to that observed previously with Pd/TiO_2 (~70%) in this temperature range. The separate roles of the palladium and V_2O_5 components of the $Pd/V_2O_5/Al_2O_3$ catalyst in the reaction mechanism are also discussed.

2. Experimental

The 10 wt% V_2O_5/Al_2O_3 support was prepared by hydrolysis of vanadium (V) oxytriisopropoxide in the presence of the alumina support, in a manner similar to that used previously to prepare mixed TiO_2/Al_2O_3 catalysts [13,14]. The resulting solid material was then

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calcined in air at 500 °C for 10 h. An XRD pattern obtained from the V_2O_3/Al_2O_3 sample at this stage displayed a profile identical to that of γ-Al_2O_3, indicating that the vanadium component was very highly dispersed. Palladium was subsequently added by impregnation with an aqueous solution of palladium (II) nitrate sufficient to yield 0.5 wt% metal loading. Following impregnation, the catalyst was dried in air overnight at 110 °C, calcined once again in air at 500 °C for 6 h and subsequently crushed/sieved to yield grain sizes in the range 255–350 μm. A 0.5 wt% Pd/Al_2O_3 catalyst was prepared in a similar manner. Metal dispersion was determined using the CO methanation technique [15], assuming a 1 : 1 CO to surface metal atom ratio. The dispersions measured were 47 and 30% for Pd/γ-Al_2O_3 and $Pd/V_2O_5/Al_2O_3$, respectively.

Catalyst testing was performed in a quartz microreactor system described previously [15]. The gas feed composition consisted of 4000 ppm H_2, 500 ppm NO and 5% O_2, delivered to the reactor with a total flow of 200 mL min^{-1}. A sample weight of 100 mg was employed, corresponding to a reciprocal weight time velocity of $w/f = 0.03$ g s mL^{-1}. Prior to testing, the samples were calcined in air (60 mL min^{-1}) for 6 h at 500 °C. The reactor outflow was analyzed using a chemiluminescence NO_x ($NO + NO_2$) analyzer (Signal 4000 series) and a dual channel NDIR detector (Siemens Ultramat 6) calibrated for NO/N_2O. Hydrogen consumption was monitored via a quadrupole mass spectrometer (Hiden RGA 301). Nitrogen production was calculated by subtracting the N_2O contribution from the total NO_x conversion. (Gas Chromatography (GC) analysis produced no evidence for NH_3 in the reactor outlet during these experiments). The catalyst temperature and all analyzer outputs were continuously monitored and recorded by a PC. Light-off profiles, typically containing 1000 data points per channel, were obtained as the catalyst temperature was raised from 50–450 °C with a linear ramp of 2 K min^{-1}.

DRIFTS experiments were performed with a Perkin–Elmer GX2000 spectrometer equipped with an MCT detector and a high-temperature, high-pressure DRIFTS cell (Thermo Spectra-Tech) fitted with ZnSe windows. Spectra were acquired at a resolution of 4 cm^{-1} typically averaging 32 scans. Background spectra were obtained from samples at the relevant temperature in a flow of 5% oxygen.

3. Results and discussion

3.1. Catalyst activity

Conversion versus temperature profiles for the reduction of NO by hydrogen (4000 ppm H_2 +500 ppm NO + 5%O_2) over the 0.5 wt% Pd/10 wt% V_2O_5/Al_2O_3 catalyst are displayed in figure 1. A maximum NO_x conversion of 95% was achieved at

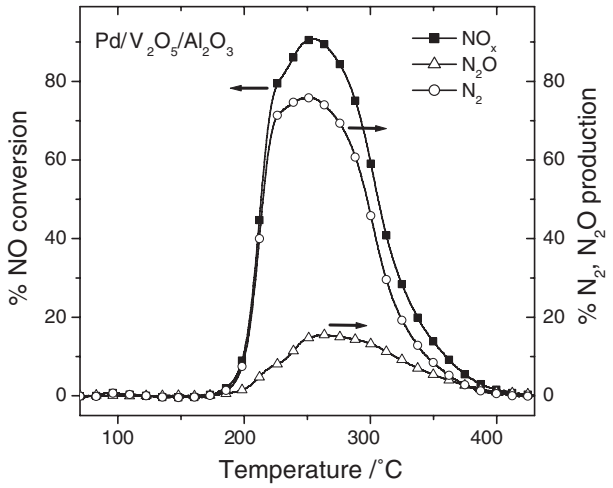

Figure 1. Total NO conversion and N_2/N_2O yields as a function of temperature during NO reduction by H_2 over $Pd/V_2O_5/Al_2O_3$ (4000 ppm H_2 + 500 ppm NO + 5%O_2).

250 °C with this sample. Under identical conditions, with the corresponding Pd/Al_2O_3 catalyst, the NO_x conversion did not exceed 10% [9]. It is therefore clear, that addition of V_2O_5 to this system strongly influences its performance. Very high NO_x conversions were maintained over a relatively wide temperature range, with > 80% conversion observed between 225 and 280 °C. The nitrogen selectivity (defined as $\%S_{N_2} = [N_2]/([N_2] + [N_2O]) \times 100$) obtained over this catalyst was also high, with $\%S_{N_2} = 81\%$ at the temperature of the conversion maximum. Although the NO_x conversion observed over $Pd/V_2O_5/Al_2O_3$ was significantly higher than that reported previously over Pd/TiO_2 ($\sim$70%) under these conditions [9], the hydrogen light-off occurred at a somewhat higher temperature on the V_2O_5 containing sample, with 100% H_2 conversion not attained until 180 °C as compared to 110 °C over Pd/TiO_2. Therefore, the low-temperature NO_x reduction pathway observed on Pd/TiO_2 was not seen with $Pd/V_2O_5/Al_2O_3$. It is important to note that when the $H_2 + NO + O_2$ reaction was carried out over a V_2O_5/Al_2O_3 sample in the absence of Pd, very low NO_x conversions were observed, indicating the key role of palladium in the reaction mechanism.

3.2. Characterization of adsorbed NO_x species by DRIFTS

DRIFT spectra obtained in a flow containing $NO + O_2$ (500 ppm NO + 5%O_2) over Pd/Al_2O_3, Pd/10 wt% V_2O_5/Al_2O_3, and V_2O_5/Al_2O_3 samples at various temperatures are shown in figure 2(a), (b), and (c), respectively. The various bands at 1615–1550 cm^{-1} and 1305–1225 cm^{-1} observed over Pd/Al_2O_3 may be assigned with confidence to the asymmetric and symmetric stretching modes respectively of variously coordinated alumina-bound nitrates [16–18]. In contrast, only very weak nitrate bands at 1595 and 1294 cm^{-1} (not

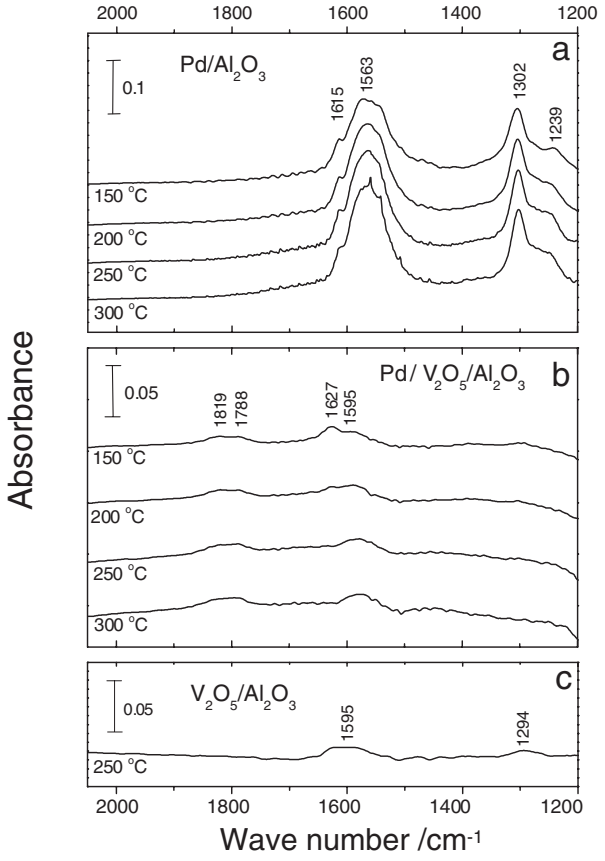

Figure 2. DRIFT spectra obtained at various temperatures in a flow containing $NO + O_2$ over (a) Pd/Al_2O_3, (b) $Pd/V_2O_5/Al_2O_3$ and (c) V_2O_5/Al_2O_3. Each temperature maintained for 1 h prior to recording spectra (500 ppm NO + 5%).

resolved in all the spectra) were observed with the 10 wt% V_2O_5/Al_2O_3 containing samples (note different scales). This indicates almost complete coverage of the alumina surface by V_2O_5 at this loading. A new band observed at 1627 cm^{-1} on the V_2O_5-containing sample is assigned to a NO_2 species adsorbed on V_2O_5 sites [19–22]. The intensity of this feature decreased as the temperature increased and it was not observed above 250 °C. On $Pd/V_2O_3/Al_2O_3$, further relatively weak bands were observed at 1819 and 1788 cm^{-1}. These bands are in the region expected for nitrosyl species. The fact that these features were not observed on the V_2O_5/Al_2O_3 sample, figure 2(c) suggests that they are related to NO adsorbed on the palladium component, with the stretching frequencies being closest to those expected for NO adsorbed on Pd^+ sites [9,19,23,24]. Note that in regard to this assignment, vanadium mono- and dinitrosyl species, which also adsorb in this frequency range, are only observed on V_2O_5-containing catalysts following reductive treatments that result in production of V^{4+} and V^{3+} sites [25–28] (V^{5+} (d^0) does not adsorb NO [19,29]). As our $Pd/V_2O_5/Al_2O_3$ catalyst was calcined in air at 500 °C prior to its contact with $NO + O_2$, the presence of reduced vanadium centers is extremely unlikely.

3.3. *DRIFTS of $Pd/V_2O_5/Al_2O_3$ under reaction conditions*

The corresponding DRIFT spectra obtained in the presence of hydrogen (4000 ppm H_2 + 500 ppm NO +5%O_2) over $Pd/V_2O_5/Al_2O_3$ are shown in figure 3. At 150–200 °C in flowing $H_2 + NO + O_2$ bands due to $Pd^+ - NO$ species (1819/1788 cm^{-1}), adsorbed NO_2 (1623 cm^{-1}) and nitrate (1587 cm^{-1}) were again observed. However, at 250 °C, the temperature of the conversion maximum in figure 1, these bands disappeared and were replaced by bands at 1660, 1625, 1420, and 1282 cm^{-1}. The bands at 1660 and 1420 cm^{-1} are assigned to the symmetric and asymmetric bending modes of NH_4^+, whilst the bands at 1625 and 1282 cm^{-1} are assigned to the corresponding deformation modes of adsorbed NH_3 [19–29, 30–32]. These assignments are confirmed by the appearance of the corresponding N-H stretching modes at 3400–3170 cm^{-1} for NH_3 and broadbands at 3020 and 2810 cm^{-1} for NH_4^+ (not shown). By comparing the intensities of the bands at 1420 and 1282 cm^{-1}, it is clear that the $Pd/V_2O_5/Al_2O_3$ catalyst contained a much greater concentration of Brønsted than Lewis acid sites.

A negative band also developed at 2045 cm^{-1} at 250 °C. This feature is assigned to the first overtone vibration of $V^{5+} = O$ groups [21,22,27,29,32,33] and is characteristic of the presence of V_2O_5. This loss of $V = O$ species under these conditions is due to their reduction by ammonia [27] (note that these spectra were obtained by ratioing with reference spectra taken in a flow of oxygen). As the temperature was raised further, the intensity of the NH_4^+ and NH_3 bands decreased, mirroring the decline in activity that occurred above 250 °C, and the $Pd^+ - NO$ bands at 1820 and 1788 cm^{-1} reappeared. At these higher temperatures, the negative

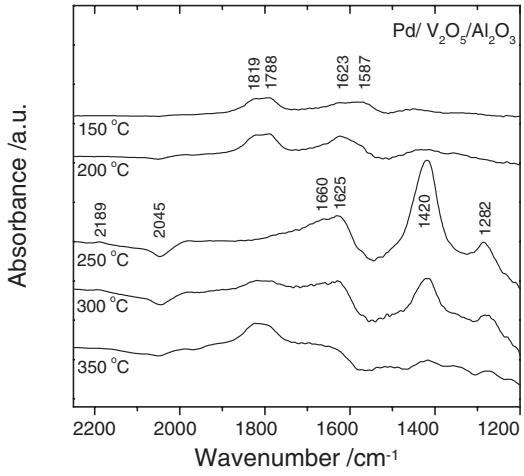

Figure 3. DRIFT spectra obtained at various temperatures in a flow containing $H_2 + NO + O_2$ over $Pd/V_2O_5/Al_2O_3$. Each temperature maintained for 1 h prior to recording spectra (4000 ppm H_2+ 500 ppm NO + 5%O_2).

peak at 2045 cm^{-1} was also removed because of reoxidation of vanadium.

To investigate the uptake and reactivity of the NH_x species, time-resolved DRIFTS studies were performed. The time-resolved spectra obtained over the $Pd/V_2O_5/Al_2O_3$ catalyst at 250 °C following the switch from a flow containing 500 ppm NO + 5%O_2 to a flow containing 4000 ppm H_2 + 500 ppm NO + 5%O_2 are shown in figure 4. The surface concentration of NH_4^+ (1660/1420 cm^{-1}) and NH_3 (1625/1288 cm^{-1}) species increased rapidly and reached steady state after ~20 min. Loss of the $Pd^+ - NO$ peaks at ~1819 cm^{-1} was observed during this time along with the appearance of the negative band at 2045 cm^{-1} associated with the removal of $V^{5+} = O$ groups. An additional weak band also developed at 2189 cm^{-1}. A similar band was observed at 2180 cm^{-1} by Ramis *et. al.* [31] following adsorption of NH_3 on a CuO/TiO_2 catalyst at room temperature and outgassing at 250 °C. This was assigned to a dinitrogen anion species, N_2^-. Adsorption of NH_3 on TiO_2 followed by outgassing to various temperatures also produced a band in this range (2197 cm^{-1}), which was again assigned to a N_2^- species [34]. However, an alternative assignment of this band to a NO^+ species is also possible [19].

Following the accumulation of the NH_x species as shown in figure 4, their reactivity toward NO + O_2 was subsequently studied by removing the H_2 component from the gas mix. The resultant time-resolved data obtained following the switch in gas feed from 4000 ppm H_2 + 500 ppm NO + 5% O_2 to 500 ppm NO + 5% O_2 are shown in figure 5. The intensity of the bands associated with both NH_3 and NH_4^+ declined very rapidly during the first 5 min following removal of hydrogen and more gradually thereafter. This indicates that both NH_3 and NH_4^+ are readily consumed in the presence of NO + O_2. It should be noted that on a corresponding Pd/TiO_2 catalyst, the major NH_x species observed under

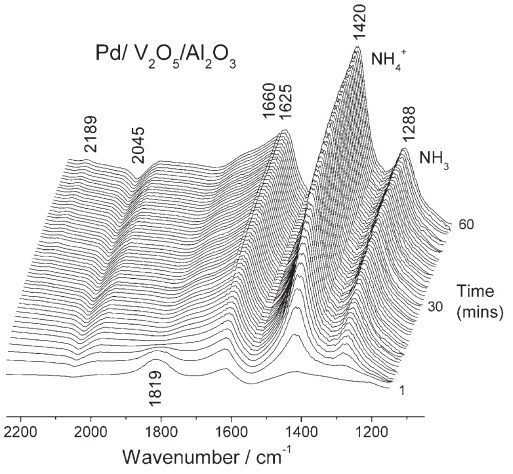

Figure 4. Time-resolved DRIFT spectra showing accumulation of NH_3 and NH_4^+ species in a flow containing H_2 + NO + O_2 flow over $Pd/V_2O_5/Al_2O_3$ at 250 °C (4000 ppm H_2 + 500 ppm NO + 5%O_2).

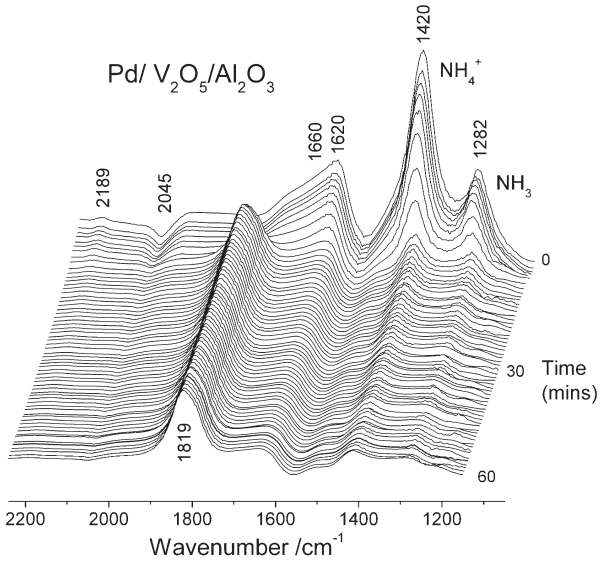

Figure 5. Time-resolved DRIFT spectra showing reactivity of NH_3 and NH_4^+ species in flowing NO + O_2 over $Pd/V_2O_5/Al_2O_3$ at 250 °C (500 ppm NO + 5%O_2).

reaction conditions was NH_3 coordinated on Lewis acid sites, with only a very minor concentration of NH_4^+ being observed [9]. Following the switch to NO + O_2, the intensity of the negative band at 2045 cm^{-1} assigned to loss of $V^{5+} = O$ groups decreased significantly, indicting reoxidation of vanadium. The weak band at 2185 cm^{-1} (N_2^- or NO^+) was also rapidly extinguished. The bands at ~1819 cm^{-1} reappeared, but with their intensity enhanced compared to that observed prior to adsorption of NH_3. This indicates an increase in the concentration of Pd^+ species following this treatment.

To elucidate the role of palladium in this system, identical time-resolved DRIFTS experiments were performed with a V_2O_5/Al_2O_3 sample. It was found that the presence of palladium was not required for NH_x generation, as both NH_3 and NH_4^+ species accumulated on the V_2O_5/Al_2O_3 sample in the presence of H_2 + NO + O_2. Figure 6 shows time-resolved spectra obtained following a switch to 500 ppm NO + 5%O_2 after the catalyst had been preconditioned in a flow containing 4000 ppm H_2 + 500 ppm NO + 5%O_2 for 1 h. Following the H_2 + NO + O_2 treatment (spectrum at $t = 0$), NH_3 and NH_4^+ species were again observed (bands at 1282/1625 cm^{-1} and 1420/1660 cm^{-1}, respectively). The negative band at 2045 cm^{-1}, which indicates loss of $V^{5+} = O$ species was also observed. However, the band at 2189 cm^{-1} (possibly N_2^-) was absent in this case, as was the 1819 cm^{-1} feature (consistent with its assignment to a $Pd^+ - NO$ species). The absence of these bands is likely to be related to the much lower activity of this sample. Comparison with figure 5 indicates that the concentration of Lewis acid sites relative to Brønsted acid sites was also somewhat diminished in the absence of palladium. Following the switch to 500 ppm NO+

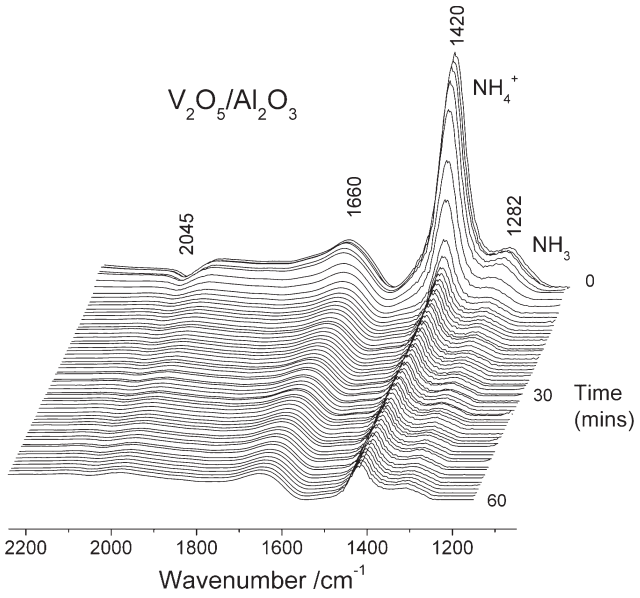

Figure 6. Time-resolved DRIFT spectra showing reactivity of NH_3 and NH_4^+ species in flowing $NO + O_2$ over V_2O_5/Al_2O_3 at 250 °C (500 ppm $NO + 5\%O_2$).

$5\%O_2$, a very rapid decline in the intensity of NH_3 and NH_4^+ species was again observed.

Although support-bound NH_3 was rapidly consumed in flowing $NO + O_2$, this purely support-mediated process was only a minor channel for NO_x conversion over the $Pd/V_2O_5/Al_2O_3$ catalyst. This is shown by the fact that the V_2O_5/Al_2O_3 control sample displayed much lower activity under these conditions. An explanation is therefore required regarding the promoting influence of palladium in this system. One possibility is that palladium promotes NO oxidation to NO_2, which subsequently reacts with adsorbed NH_x species. It was observed, however, that whenever NH_x were present on the V_2O_5/Al_2O_3 surface, the corresponding $Pd^+ - NO$ bands were removed (figures 3, 4, and 5). This may indicate rapid consumption of NO adsorbed on palladium sites by reaction with the NH_x species generated on the support. The role of the noble metal may, therefore, be to catalyze this $NO + NH_x$ reaction. The participation of palladium in this process explains why the concentration of N_2O produced, although relatively small, is still significantly higher than observed during conventional NH_3 SCR over V_2O_5/Al_2O_3 [3,4].

4. Conclusions

1. $Pd/V_2O_5/Al_2O_3$ catalysts deliver very high NO_x conversions (>90%) in the presence of $H_2 + NO + O_2$ under oxygen-rich conditions. Very good nitrogen selectivity is also obtained (~80%).

2. The high activity is related to *in situ* formation of NH_x species. Both NH_3 and NH_4^+ species are observed, with the latter dominant.

3. The formation of NH_x species occurs on the V_2O_5 component and does not involve participation of the noble metal. This support-generated NH_x is able to react with NO species adsorbed on palladium sites.

References

[1] V.I. Pârvulescu, P. Grange and B. Delmon, Catal. Today 46 (1998) 233.
[2] A. Fritz and V. Pitchon, Appl. Catal., B 13 (1997) 1.
[3] G.T. Went, L.J. Leu, R.R. Rosin and A.T. Bell, J. Catal. 134 (1992) 492.
[4] G. Busca, L. Lietti, G. Ramis and F. Berti, Appl. Catal., B 18 (1998) 1.
[5] M. Koebel, M. Elsener and M. Kleemann, Catal. Today 59 (2000) 335.
[6] L.F. Xu, R.W. McCabe and R.H. Hammerle, Appl. Catal., B 39 (2002) 51.
[7] E. Seker, N. Yasyerli, E. Gulari, C. Lamert and R.H. Hammerle, Appl. Catal., B 37 (2002) 27.
[8] J.P. Breen, R. Burch and N. Lingaiah, Catal. Lett. 79 (2002) 171.
[9] N. Macleod, R. Cropley and R.M. Lambert, Catal. Lett. 86 (2003) 69.
[10] A. Ueda, N. Takayuki, A. Masashi and T. Kobayashi, Catal. Today 45 (1998) 135.
[11] A. Ueda, T. Nakao, M. Azuma and T. Kobayashi, Chem. Lett. (1998) 595.
[12] R. Burch and M.D. Coleman, J. Catal. 208 (2002) 435.
[13] N. Macleod and R.M. Lambert, Catal. Commun. 3 (2002) 61.
[14] N. Macleod, R. Cropley, J.M. Keel and R.M. Lambert, submitted to J. Catal.
[15] N. Macleod, J. Isaac and R.M. Lambert, J. Catal. 193 (2000) 115.
[16] W.S. Kijlstra, D.S. Brand, E.K. Poels and A. Bliek, J. Catal. 171 (1997) 208.
[17] F.C. Meunier, J.P. Breen, V. Zuzaniuk, M. Olsson and J.R.H. Ross, J. Catal. 187 (1999) 493.
[18] S. Kameoka, Y. Ukisu and T. Miyadera, Phys. Chem. Chem. Phys. 2 (2000) 367.
[19] K.I. Hadjiivanov, Catal. Rev.–Sci. Eng. 42 (2002) 71.
[20] R.Q. Long and R.T. Yang, J. Catal. 196 (2000) 73.
[21] M.A. Centeno, I. Carrizosa and J.A. Odriozola, Phys. Chem. Chem. Phys. 1 (1999) 349.
[22] N.Y. Topsøe, H. Topsøe and J.A. Dumesic, J. Catal. 151 (1995) 226.
[23] T. Maillet, J. Barbier, P. Gelin, H. Praliaud and D. Duprez, J. Catal. 202 (2001) 367.
[24] K. Almusaiteer and S.S.C. Chuang, J. Catal. 184 (1999) 189.
[25] H. Miyata, S. Konishi, T. Ohno and F. Hatayama, J. Chem. Soc. Faraday Trans. 9 (1995) 1557.
[26] N.Y. Topsøe, J. Catal. 128 (1991) 499.
[27] M.A. Centeno, I. Carrizosa and J.A. Odriozola, Appl. Catal., B 29 (2001) 307.
[28] H. Schneider, S. Tschudin, M. Schneider, A. Wokaun and A. Baiker, J. Catal. 147 (1994) 5.
[29] H. Kamata, K. Takahashi and C.U.I. Odenbrand, J. Catal. 185 (1999) 106.
[30] G. Ramis, G. Busca, V. Lorenzelli and P. Forzatti, Appl. Catal., 64 (1990) 243.
[31] G. Ramis, L. Yi, G. Busca, M. Turco, E. Kotur and R.J. Willey, J. Catal. 157 (1995) 523.
[32] M.A. Centeno, I. Carrizosa and J.A. Odriozola, Appl. Catal., B 19 (1998) 67.
[33] N.Y. Topsøe, H. Topsøe and J.A. Dumesic, J. Catal. 151 (1995) 241.
[34] J.M.G. Amores, V.S. Escribano, G. Ramis and G. Busca, Appl. Catal., B 13 (1997) 45.