Journal of Catalysis **209,** 159–165 (2002)
doi:10.1006/jcat.2002.3624

Enhanced Reoxidation of Vanadia by NO_2 in the Fast SCR Reaction

Manfred Koebel,[1] Giuseppe Madia, Fabio Raimondi, and Alexander Wokaun

Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland

Received November 26, 2001; revised March 25, 2002; accepted March 28, 2002

The rate of the selective catalytic reduction of NO with N-containing reducing agents may be considerably enhanced by converting part of the NO into NO_2. The reaction using an equimolar mixture of NO and NO_2 is known as "fast SCR reaction" and the rate enhancement is most pronounced at low temperatures ($T < 300°C$). In the present study the possible role of NO_2 on catalysts based on TiO_2–WO_3–V_2O_5 was investigated. Transient experiments in a test reactor and *in situ* Raman spectroscopy investigations were performed to study the reoxidation of the vanadium species in the catalyst. The experiments suggest that the V^{+4} species formed during the reduction of NO with ammonia are reoxidized faster by NO_2 than by oxygen, resulting in an increased reaction rate of the fast SCR reaction.

1. INTRODUCTION

Among the various selective DeNOx techniques currently under investigation that have the potential of meeting future European and U.S. emission standards of diesel-powered vehicles, the urea SCR technique is the most promising for maturing into a commercial process (1–6). This is true especially for heavy-duty vehicles like trucks and buses due to their high average exhaust gas temperatures and the required high fuel economy. For diesel passenger cars other DeNOx techniques, such as HC-SCR or NO_x storage reduction catalysts, are also being discussed (7, 8).

The main requirements for an SCR catalyst of automotive applications are high volumetric activity, stability over a wide temperature range (180–650°C), and high selectivity with respect to the SCR reaction. In the last years, a main challenge was the development of catalysts with higher volumetric activity and this has been achieved by increasing the intrinsic activity of the catalyst formulation and by increasing the cell density of the monoliths (9). Besides measures aiming at increasing the volumetric activity of the SCR catalyst itself, it has been found that utilizing the "fast SCR" reaction is another means of increasing SCR performance, especially at low temperatures (1, 5, 6). Introducing a strong oxidation catalyst (Pt based) upstream of the SCR catalyst will increase the fraction of NO_2 in the exhaust and this allows for the occurrence of the "fast SCR reaction" according to

$$4NH_3 + 2NO + 2NO_2 \rightarrow 4N_2 + 6H_2O. \qquad [1]$$

The beneficial effect of the fast SCR reaction on the overall conversion of NO_x for a given SCR catalyst has been reported by various authors (1–3, 5, 6). It is noted that the NO fraction in diesel exhaust is usually higher than 90%, so that the main reaction occurring on an SCR catalyst will be the "standard SCR reaction":

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O. \qquad [2]$$

In a recent publication (6) we reported detailed experiments with NO–NO_2 mixtures and ammonia at low temperatures using a TiO_2–WO_3–V_2O_5-based catalyst. We have proposed a reaction mechanism for fast SCR in which NO_2 would be responsible for the faster reoxidation of V^{+4} sites produced in a preceding step of the SCR mechanism. The present work aims at proving this hypothesis by following the reoxidation of V^{+4} centers by two different experimental techniques: transient experiments in a test reactor and *in situ* Raman spectroscopy. The formation of V^{+5} species by oxidation of V^{+4} centers can be monitored directly by *in situ* Raman spectroscopy, since the V=O groups associated with V^{+5} ions in the vanadia lattice give rise to strong Raman bands in the range between 850 and 1030 cm^{-1}. In order to avoid the interference of the Raman bands corresponding to the W=O stretching, the *in situ* Raman spectroscopy experiments were carried out on a W-free TiO_2–V_2O_5-based catalyst.

2. EXPERIMENTAL

Reactor and Catalysts

A tubular glass reactor of 30 mm inner diameter and about 500 mm in length was used. The reactor includes a preheating zone of 150 mm and is heated by two separate temperature-controlled heating coils. Two different monolithic catalyst samples based on TiO_2–WO_3–V_2O_5 were

---

[1] To whom correspondence should be addressed. E-mail: manfred.koebel@psi.ch.

0021-9517/02 $35.00

TABLE 1

Catalyst Specifications and Test Conditions

Specification	Units	D42B	M11
Cell density	cells/inch^2	300	600
V_2O_5	wt%	≈3	≈3
WO_3	wt%	≈8	≈8
BET	m^2/g	55	75
Pore volume	cm^3/g	0.21	0.27
Av. pore diameter	Å	141	131
Sample volume	cm^3	8.3	7.3
Active mass	g	5.23	1.4
Gas volume flow	cm^3_N/h	432,000	380,000
GHSV	1/h	52,000	52,000

used. One was a commercial extruded catalyst (D42B from Ceram, Frauenthal) and the other was a coated catalyst on a metallic substrate (M11) prepared in-house according to (9). Further specifications are given in Table 1.

Feed Gas

The composition of the feed gas used in the experiments was adapted to a typical exhaust gas, i.e., the "base feed" contained 10% oxygen and 5% water, with the overall balance being nitrogen. NO, NO_2, and NH_3 were in the range 200–1500 ppm. The feed gas was mixed from gas mixtures of higher concentration using mass flow controllers (Brooks). Water was dosed in liquid form into an electrically heated evaporator. The gas lines to the reactor and to the FTIR spectrometer were heated to 150°C. More details on the experimental setup, including a drawing, have been given previously (10).

Gas Analysis

Multicomponent gas analysis was performed by means of an FTIR spectrometer (Nicolet Magna IR 560, OMNIC® QuantPad software) equipped with a multiple pass gas cell (Graseby Specac G-2-4-BA-AU; path length, 2 m) and a liquid-nitrogen-cooled MCT detector. The method developed allowed the simultaneous determination of NO, NO_2, N_2O, HNO_3, NH_3, and H_2O.

Influence of Oxygen

The influence of oxygen on the NO_x conversion was tested in a steady state type experiment with catalyst M11 at three temperatures (200, 250, 300°C) and a flow rate of 380 l_N/h. The NO_x conversion at steady state was measured for various oxygen concentrations in the feed. The feed contained 0–20% O_2, 5% H_2O, 1000 ppm NH_3, 1000 ppm NO_x, and balance nitrogen. NO_x consisted of 1000 ppm NO in the case of standard SCR and of 500 ppm each NO and NO_2 in the case of fast SCR.

Transient Experiments

The catalyst sample (D42B) was pretreated in the reactor at 450°C in flow of 10% $O_2 + 5\%\ H_2O$, balance N_2, for 1 h. Subsequently it was reduced at 300°C in a feed gas consisting of 1000 ppm NO, 1000 ppm NH_3, 5% H_2O, balance N_2, for 30 min. Due to the absence of oxygen in the feed and considering reaction [2], the catalyst will be reduced ($V^{+5} \rightarrow V^{+4}$), i.e., the required oxygen will be taken from the V_2O_5 lattice. In the next step, adsorbed NH_3 was removed by heating the catalyst to 450°C in a stream of 5% $H_2O + N_2$. A first reoxidation experiment was then performed at 300°C with a feed containing 345 ppm NO_2, 5% water, balance N_2, at a flow rate of 432 1_N/h. A second reoxidation experiment was made with a feed containing also 350 ppm NH_3. This experiment was repeated with a catalyst not previously reduced.

In Situ Raman Spectroscopy Experiments

Raman spectra were collected using a confocal Raman microscope (Labram, DILOR) equipped with a 50× magnification objective (laser spot size $\approx 5\ \mu m$) and a thermoelectrically cooled CCD detector (1152 × 300 pixels). The Raman spectra were obtained in a backscattering geometry with the yellow line ($\lambda = 568.2$ nm) of a Kr-ion laser (Coherent Innova 302). The power at the sample was kept at 2.0 ± 0.1 mW. No sample degradation occurred after prolonged exposure to this laser power, as shown by the constancy of the Raman spectra with acquisition time. Raman spectra were routinely acquired in the range from 250 to 1500 cm^{-1} using a 1800 grooves/mm grating. The catalyst treatments were carried out in a Linkam T1500 heated stage equipped with a quartz window for the collection of *in situ* Raman spectra.

3. RESULTS AND DISCUSSION

Influence of Oxygen on the Standard and the Fast SCR Reaction

Figure 1 shows the stationary NO_x conversion ("DeNOx") of the standard SCR reaction (NO_x in the feed = pure NO) as a function of oxygen in the feed. If the feed contains no oxygen, the DeNOx is zero at all three temperatures. It can be seen that oxygen accelerates the reaction at all three temperatures. However, the influence of oxygen concentration is different for the three temperatures. At the lower temperatures of 200 and 250°C, the DeNOx still increases with oxygen concentration at 20% oxygen. This is no longer true at 300°C, where the DeNOx is virtually independent of oxygen concentration above ≈4% oxygen.

We should add that the consumption of NH_3 and NO corresponds to a 1 : 1 ratio. Therefore, possible side reactions can virtually be excluded. The maximum amount of N_2O was 2 ppm at 300°C, and HNO_3, although accessible by the

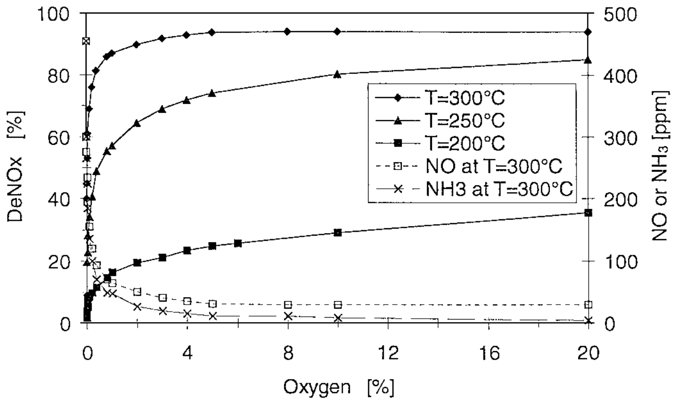

FIG. 1. DeNOx vs O_2 concentration. Feed: 1000 ppm NO, 1000 ppm NH_3, 5% H_2O, O_2 varied, balance N_2.

used method, could not be detected. A slight oxidation of NH_3 to N_2 may only be suspected at the highest temperature, 300°C, due to a slight excess consumption of NO over NH_3. The corresponding concentrations of NO and NH_3 in the efflux are also reported in Fig. 2. However, this excess consumption is below 3% of the total amount of reacted NO, a number which is even within the limits of precision of the experiment.

These results suggest that oxygen is rate limiting for the standard SCR reaction only at temperatures below 300°C and this may well be due to depletion of lattice oxygen or reduction of V. Other researchers have also found evidence that the reoxidation of V may be rate limiting at low temperatures (15–17). The direct oxidation of NO to NO_2 in the absence of NH_3 has also been measured and found to be negligible: 1% at 200°C, 1.4% at 250°C, 1.8% at 300°C, and 2.3% at 350°C. Therefore, a relevant enhancement of the NO_x conversion due to the fast SCR reaction can be excluded.

The results are also in full agreement with previous investigations on the fast SCR reaction (21). Figure 2 of this paper demonstrates that the fast SCR reaction [1] using the equimolar mixture of $NO + NO_2$ is most effective at temperatures below 300°C. At 300°C the difference between the fast SCR and the standard SCR reaction becomes marginal and this difference even vanishes above 350°C.

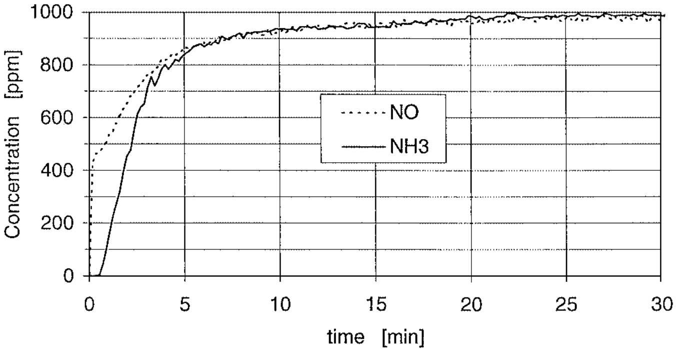

FIG. 2. Reduction of catalyst D42B. Feed: 1000 ppm NO, 1000 ppm NH_3, 5% H_2O, balance N_2.

Analogous experiments have been carried out to test the influence of oxygen on the fast SCR reaction. In this case, NO_x in the feed consisted of 500 ppm $NO + 500$ ppm NO_2. At all three temperatures, no influence of oxygen concentration on DeNOx could be found. The conversion was 91% at 200°C, and practically 100% at both 250 and 300°C. This proves that the fast SCR reaction does not involve gaseous oxygen.

Transient Experiments to Study the Reoxidation of the Catalyst

Figure 2 shows the concentrations of NO and NH_3 at the reactor outlet during the reduction of the catalyst in a feed without oxygen. The rise in ammonia concentration shows a delay of about 1 min due to its adsorption on the catalyst. The concentrations of both NH_3 and NO rise slowly up to their values in the feed. This implies that initially the SCR reaction takes place at an appreciable rate, consuming oxygen from the V_2O_5 lattice, and thereby reducing steadily the V^{+5} sites. After consumption of all available lattice oxygen the SCR reaction ceases.

The amount of reducible V sites on the catalyst can be evaluated from the amount of NO reacted in the process, making the following assumptions:

1. According to reaction [2], each molecule of NO reacted consumes 0.25 O_2 corresponding to one electron. This electron is transferred to V^{+5}, thus yielding V^{+4}. Assuming that the reduction does not proceed further to V^{+3}, the amount of NO consumed corresponds to the number of V^{+5} sites reduced in the experiment.
2. The rate of the following reaction without oxygen is practically zero at the actual conditions ($T = 300°\text{C}$, $\text{GHSV} = 52000\ \text{h}^{-1}$):

$$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O. \quad [3]$$

The fact that the outlet concentrations of NO and NH_3 approach their inlet values when the catalyst is completely reduced proves that this assumption is correct. From a quantitative analysis of the curve of NO concentration in Fig. 2, the amount of the reduced V sites of the catalyst sample can be calculated to be 0.84 mmol.

Figure 3 shows the results of the reoxidation of the catalyst by NO_2 in terms of concentrations of NO and NO_2 at the reactor outlet vs time (after the reported thermal stripping of adsorbed ammonia). The reoxidation of the V^{+4} sites by NO_2 leads to the formation of NO, which is detected at the reactor outlet. The quantitative analysis of the curves in Fig. 3 shows that the amount of NO detected at the reactor outlet corresponds to the amount of NO_2 consumed in the

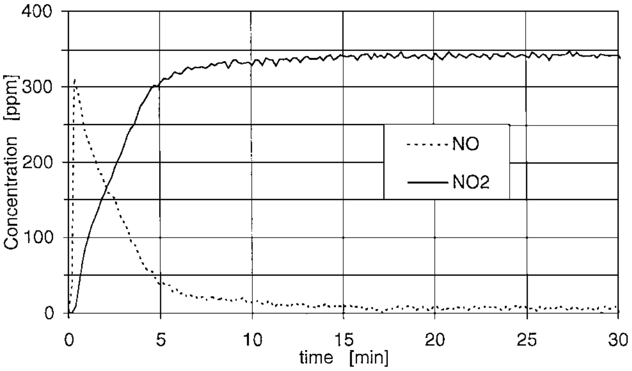

FIG. 3. Reoxidation of catalyst D42B. Feed: 345 ppm NO_2, 5% H_2O, balance N_2.

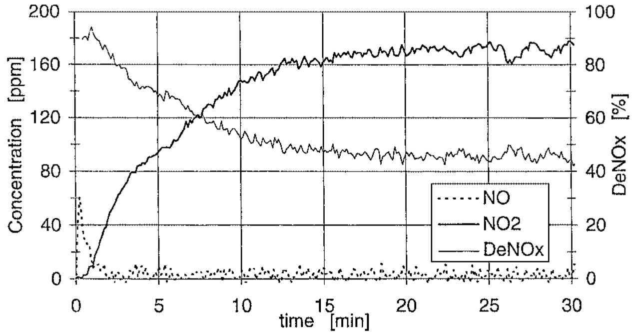

FIG. 4. Reoxidation of catalyst D42B. Feed: 320 ppm NO_2, 350 ppm NH_3, 5% H_2O, balance N_2.

process (0.35 mmol). From these considerations, we propose the following scheme for the reoxidation of the V^{+4} sites by NO_2:

$$2V^{+4}OH + NO_2 \rightarrow 2V^{+5}{=}O + NO + H_2O. \qquad [4]$$

According to this reaction the number of the V^{+4} sites is twice the amount of NO produced in the reoxidation: $2 \cdot 0.35 = 0.7$ mmol. This value is close to the value of 0.84 mmol obtained previously considering the amount of NO consumed during the reduction of the catalyst. The difference between the two values should be attributed to the limited precision of the NO measurement and to the likely adsorption of ammonia, the latter being also a reducing agent.

These values should be compared with the total amount of V sites in the sample, which amounts to 1.72 mmol. Evidently, not all vanadia sites are reduced to V^{+4} before the activity drops. Assuming an average value of 0.75-mval exchanged redox equivalents, the formal change in the oxidation number of vanadium is −0.44. Also the Raman experiments reported below yield only a fractional reduction of the V sites, −0.35 (−0.75/1.72). This observation, that not all V^{+5} sites are reduced to V^{+4} (or all V^{+5} sites are reduced to some intermediate value), is remarkable and merits attention in future experiments.

If ammonia is present together with NO_2 during the reoxidation phase, the situation becomes more complex. NO formed in reaction [4] will react with NO_2 and NH_3 on the catalyst according to the fast SCR reaction [1]. Therefore, the amount of NO detected at the reactor outlet is much lower than the amount formed according to [4] and additional NO_2 is consumed in the fast SCR reaction. Figure 4 shows results during the reoxidation of the catalyst with a stream containing NH_3 and NO_2. After ≈15 min, the concentration of NO_2 approaches a stationary value. The difference between the NO_2 concentration in the feed and the stationary value is the amount consumed according to the SCR reaction involving NO_2 only:

$$4NH_3 + 3NO_2 \rightarrow 3.5N_2 + 6H_2O. \qquad [5]$$

Figure 4 reports also the DeNOx vs time for this experiment. The DeNOx vs time curve falls gradually to a stationary value, which is reached after about 15 min. The stationary value is due to the SCR reaction [5] with pure NO_2. The decrease of DeNOx with time can be explained as follows: At the beginning, NO_2 not only reacts with NH_3 but also reoxidizes the V^{+4} sites, thereby forming NO. This NO reacts with NH_3 and NO_2 according to the fast SCR reaction [1]. Consequently, the DeNOx is initially high, then decreases with time as the V^{+4} sites are oxidized. In the steady state only reaction [5] occurs, and the DeNOx corresponds to the conversion of NO_2 in this reaction. Due to the fact that both V^{+4} and NH_3 consume NO_2 a quantitative determination of the V^{+4} sites is not possible. However, the experiment shows that the reoxidation of the V^{+4} sites with NO_2 occurs even in the presence of ammonia.

The above experiment was repeated with an oxidized SCR catalyst (Fig. 5). In this case the concentration of NO_2 at the reactor outlet and the DeNOx approach the steady-state values much faster but the final values correspond reasonably to those observed upon reoxidation of the

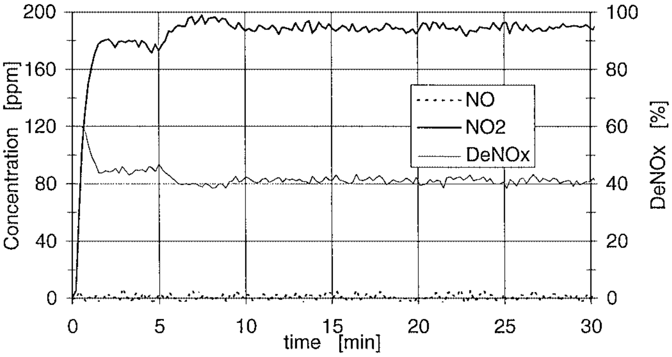

FIG. 5. Experiment on catalyst D42B not previously reduced. Feed: 320 ppm NO_2, 350 ppm NH_3, 5% H_2O, balance N_2.

reduced catalyst (Fig. 4). This confirms that the transient in the values of DeNOx and in the outlet concentration of NO_2 reported in Fig. 4 are due to reaction [4].

The oxidation–reduction experiments and vice versa have been repeated using the same sample. The results suggest that the redox process is reversible.

In Situ Raman Experiments

For the *in situ* Raman spectroscopy investigations, a TiO_2–V_2O_5 powdered catalyst was prepared in house according to the recipe described in (9), omitting WO_3. A fraction of 160- to 200-μm particle size was used after calcination at 500°C for 4 h. After positioning into the Raman cell, the sample was heated to 500°C (30°C/min) in a flow of 900 ppm NH_3/N_2 (30 ml/min, atmospheric pressure) and kept at this temperature for 20 min. Then the cell was flushed with N_2 for 10 min in order to desorb NH_3 from the catalyst and cooled to ambient temperature. The result of this reducing treatment was a drop of the intensity of the V=O stretching bands in the region 850–1030 cm^{-1} to 0.65 times its original value, due to the partial conversion of V^{+5}=O groups to V^{+4}–OH groups. The residual intensity of the V=O stretching bands after reduction indicates that not all V^{+5} centers present in the catalyst can be reduced to V^{+4} by the applied treatment. Finally, the oxidizing mixture (synthetic air or 900 ppm NO_2 in N_2) was fed to the cell at a flow of 30 ml/min and after 15 min a 4°C/min heating ramp up to 500°C was started. While heating, one Raman spectrum every 2 min was acquired. In order to follow the reoxidation of V^{+4}–OH groups to V^{+5}=O groups in a quantitative manner, the Raman spectra were baseline corrected, by subtracting the second-order polynomial that fitted the 1200- to 1500-cm^{-1}-region best, and deconvoluted using Gaussian–Lorentzian curves. The positions of the peaks used in the fitting procedure and their assignment are listed in Table 2. The Raman spectra of the calcined catalyst before and after data treatment are shown in Fig. 6. The sum of the area of the V^{+5}=O stretching peaks (continuous lines in Fig. 6b) was normalized using the area of the V^{+5}=O stretching bands of the freshly calcined catalyst, and its variation with temperature during reoxidation was considered.

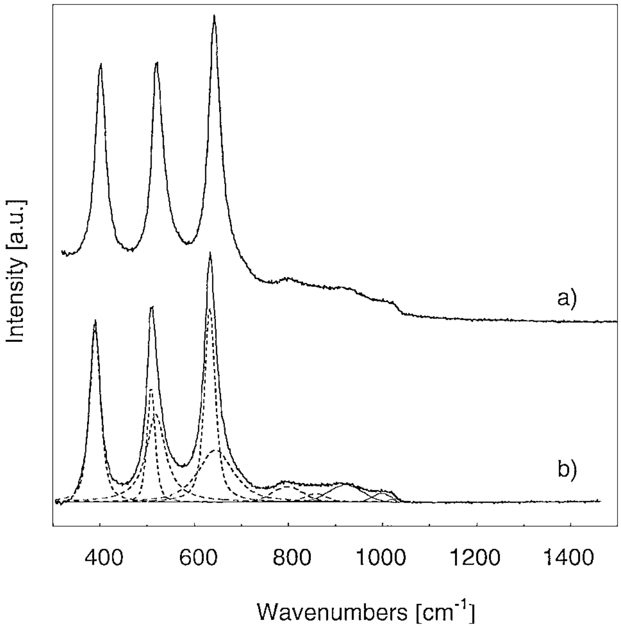

FIG. 6. Raman spectrum of the calcined catalyst. (a) As measured; (b) after baseline correction and band deconvolution (see text). Dashed lines, Anatase peaks and V–O–V stretching bands; continuous lines, V=O stretching bands.

TABLE 2

Spectral Components Used to Fit the Baseline-Corrected Raman Spectra

Peak position (cm^{-1})	Assignment	Reference
397	Anatase	11
512	Anatase	11
519	Anatase	11
636	Anatase	11
645	Anatase	11
799	Anatase	12
857	V–O–V stretch	13
921	V=O stretch	14
990	V=O stretch	14
1020	V=O stretch	14

Figure 7 shows the variation of the total area of the V^{+5}=O stretching bands with temperature during the oxidation of a TiO_2–V_2O_5 catalyst previously reduced with

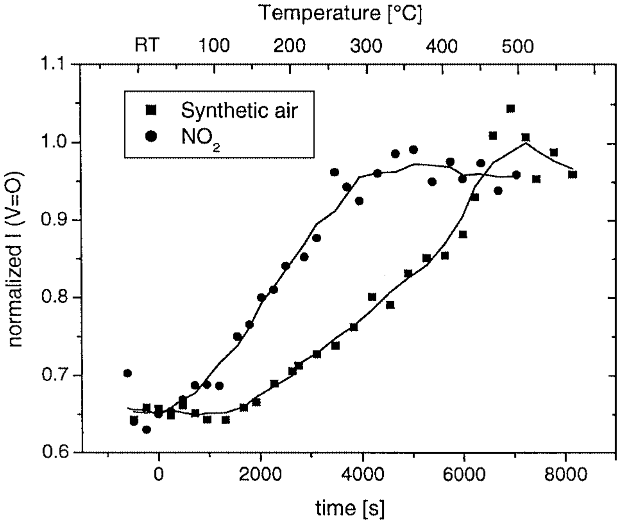

FIG. 7. Variation of the normalized intensity of the V=O stretching bands (sum of all areas) with temperature during reoxidation in synthetic air (squares) and 900 ppm NO_2/N_2 (circles). The black lines are obtained by adjacent point smoothing of the data. Heating rate = 4°C/min. The ramp was started at t = 0 s (T = 22°C) and was stopped after 7080 s (T = 500°C). Negative times refer to spectra acquired before the beginning of the heating ramp.

NH_3. Two different oxidation treatments were carried out: one with synthetic air, the other with 900 ppm NO_2/N_2. With both oxidizing mixtures the intensity of the $V^{+5}{=}O$ increases with increasing temperature, indicating that new $V^{+5}{=}O$ groups are formed by oxidation of V^{+4} centers. The slope of the $I(V{=}O)$ vs T curve corresponding to reoxidation with the NO_2-containing mixture is higher, suggesting that the oxidation of V^{+4} centers with 900 ppm NO_2/N_2 is faster than the corresponding reaction with air. The slope of the linear part of the normalized $I(V{=}O)$ vs T curves was calculated from three replicated experiments with each oxidizing agent. Standard deviations of 5 and 15% were observed in the case of 900 ppm NO_2/N_2 and synthetic air, respectively. After both reoxidation treatments the intensity of the $V^{+5}{=}O$ stretching bands reached the value measured for the freshly calcined catalyst. This indicates that both applied treatments fully reoxidize the V^{+4} centers.

It is theoretically possible to extract from the $I(V{=}O)$ vs T plots in Fig. 7 the kinetic parameters of the oxidation of V^{+4} centers with NO_2 and air. However, this operation is complicated by two facts. First, the temperature of the area of the catalyst generating the detected Raman signal might be significantly different from the one of the surrounding material, due to the heat developed by the absorption of the laser beam. Second, the relation between the intensity of the sum of the $V{=}O$ stretching bands and the amount of V^{+5} centers in the catalyst is of a complex nature. As a matter of fact it is well-known that the intensity of the $V{=}O$ stretching bands is strongly influenced by a number of structural properties, e.g., the degree of polymerization of the V^{+5} centers, as well as the degree of hydration and the crystallinity of the vanadium oxide phase (14, 18).

However these complications do not prevent a qualitative use of the plots in Fig. 7. Since all experimental parameters (e.g., laser power, heating rate, grain size) were the same during the reoxidation treatments with 900 ppm NO_2/N_2 and with air, it can be safely assumed that the temperature deviation of the laser-irradiated spot was the same for both experiments. In other words, the temperature scale in Fig. 7 might not reflect the actual temperature of the laser-irradiated spot during the reoxidation ramp, but it is surely the same for both curves. Similarly, a significant influence of a different evolution of the structural properties listed above on the shape of the $I(V{=}O)$ vs T curves for the two oxidizing agents is not likely. This is supported by the fact that the $V{=}O$ intensity at the end of both reoxidation treatments is the same, indicating that the chosen oxidizing agent has no influence on the structural properties of the completely oxidized vanadium oxide obtained at the end of the heating ramps. It is plausible that such a lack of influence of the specific oxidizing agent on the structural properties of the catalyst is valid at any stage of the oxidation treatment and that the intensity of the $V{=}O$ stretching bands is related to the amount of V^{+5} present in the catalyst in the same way for both oxidizing agents. Therefore, it can be concluded that the steeper increase of $I(V{=}O)$ observed during treatment with the NO_2/N_2 mixture is a direct indication of a faster oxidation of V^{+4} sites with 900 ppm NO_2/N_2 than with air.

Proposed Reaction Mechanism

The rate of NO_x conversion of the standard SCR reaction is influenced by the presence of oxygen at temperatures below 300°C. This implies that oxygen is involved in the rate-determining step of this reaction under these conditions. On the other hand, the fast SCR reaction does not depend on oxygen concentration and even proceeds in the absence of oxygen, indicating that oxygen is not involved in the mechanism of this reaction. At temperatures below 300°C the fast SCR reaction is faster than the standard SCR reaction, whereas the rates of both reactions converge at higher temperatures. These observations can be accounted for assuming that in the fast SCR reaction NO_2 plays the role of oxygen, speeding up the rate-limiting step at low temperatures. The mechanisms proposed for the standard SCR reaction (19, 20) postulate that oxygen is essential for the reoxidation of the vanadium sites of the catalyst. In the case of the fast SCR reaction this role is played by NO_2 in a much more efficient way. The Raman experiments have confirmed that NO_2 reoxidizes the vanadium sites faster than oxygen, thus explaining the higher rate of the fast SCR reaction at low temperatures. Furthermore, transient experiments have shown that one molecule of NO is formed for each molecule of NO_2 consumed in the reoxidation of the vanadium sites. From these observations, we propose a mechanism for the fast SCR reaction similar to the one suggested by Ramis *et al.* (19) for the standard SCR reaction.

$$V^{+5}{=}O + NH_3 \rightarrow HO{-}V^{+4}{-}N^{\bullet}H_2 \quad [I]$$

$$HO{-}V^{+4}{-}N^{\bullet}H_2 + {}^{\bullet}NO \rightarrow HO{-}V^{+4}{-}(NH_2){-}NO \quad [II]$$

$$HO{-}V^{+4}{-}(NH_2){-}NO \rightarrow HO{-}V^{+4} + N_2 + H_2O \quad [III]$$

$$2HO{-}V^{+4} + NO_2 \rightarrow 2V^{+5}{=}O + {}^{\bullet}NO' + H_2O \quad [IV]$$

$$V^{+5}{=}O + NH_3 \rightarrow HO{-}V^{+4}{-}N^{\bullet}H_2 \quad [I']$$

$$HO{-}V^{+4}{-}N^{\bullet}H_2 + {}^{\bullet}NO' \rightarrow HO{-}V^{+4}{-}(NH_2){-}NO' \quad [II']$$

$$HO{-}V^{+4}{-}(NH_2){-}NO' \rightarrow HO{-}V^{+4} + N_2 + H_2O \quad [III']$$

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O \quad [6]$$

where ${}^{\bullet}NO' = {}^{\bullet}NO$ formed from NO_2 in [IV].

This reaction mechanism differs only in the reoxidation step [IV] from the mechanism proposed by Ramis *et al.* (19) for the standard SCR reaction. Therefore, the fast SCR reaction can be considered as a standard SCR reaction in which NO_2 plays the role of supplying more reactive oxygen for the reoxidation of the catalyst.

The proposed mechanism requires equimolar amounts of NO and NO_2. This is in accordance with the observations reported in previous publications (6, 21), where it has been found that the equimolar mixture yields the highest conversions (or rates) at low temperatures. Any excess of NO has to react according to the standard SCR reaction [2], and any excess of NO_2 has to react according to the SCR reaction involving NO_2 only (reaction [5]). Both reactions are slower than the fast SCR reaction.

4. CONCLUSIONS

The reoxidation of the vanadium sites is the rate-limiting step in the standard SCR reaction at temperatures below 300°C. In the fast SCR reaction NO_2 is very effective in speeding up this critical step. The faster reoxidation of the vanadium sites by NO_2 allows an increase in the reaction rate of the SCR process at low temperatures. The fast SCR reaction can be considered as a standard SCR reaction in which NO_2 plays the role of a more efficient oxidizer for the vanadium sites.

ACKNOWLEDGMENT

The financial support of the Swiss Federal Office of Energy (BFE) is gratefully acknowledged.

REFERENCES

1. Jacob, E., Emmerling, G., Döring, A., Graf, U., Harris, M., van den Tillaart, J. A. A., and Hupfeld, B., *in* "19th International Vienna Motor Symposium, May 7–8, 1998," Bd. 1, p. 366. VDI-Verlag, Düsseldorf.
2. Gieshoff, J., Schäfer-Sindlinger, A., Spurk, P. C., van der Tillaart, J. A. A., and Garr, G., *Improved SCR Systems for Heavy-Duty Applications*, SAE 2000-01-0189 (2000).
3. Chandler, G. R., Cooper, B. J., Harris, J. P., Thoss, J. E., Uusimäki, A., Walker, A. P., and Warren, J. P., *Integrated SCR and Continuously Regenerating Trap System to Meet Future NOx and PM Legislation*, SAE 2000-01-0188 (2000).
4. Hofmann, L., Mathes, W., and Fischer, S., *in* "20th International Vienna Motor Symposium, May 6–7, 1999," p. 267. VDI-Verlag, Düsseldorf.
5. Koebel, M., Elsener, M., and Kleemann, M., *Catal. Today* **59**, 335 (2000).
6. Koebel, M., Elsener, M., and Madia, G., *Ind. Chem. Eng. Res.* **40**, 52 (2001).
7. Shelef, M., *Chem. Rev.* **95**, 209 (1995).
8. Fridell, E., Skogludh, M., Westerberg, B., Johansson, S., and Smedler, G., *J. Catal.* **183**, 196 (1999).
9. Kleemann, M., Dissertation Nr. 13401, ETH Zurich, 1999.
10. Kleemann, M., Elsener, M., Koebel, M., and Wokaun, A., *Ind. Eng. Chem. Res.* **39**, 4120 (2000).
11. Bersani, D., Lottici, P. P., Braghini, M., and Montenero, A., *Phys. Status Solidi B* **K5**, 170 (1992).
12. Chan, S. S., Wachs, I. E., Murrel, L. L., Wang, L., and Hall, W. K., *J. Phys. Chem.* **88**, 5831 (1984).
13. Alemany, L. J., Lietti, L., Ferlazzo, N., Busca, G., Giamello, E., and Bregani, F., *J. Catal.* **155**, 117 (1995).
14. Went, G. T., Leu, L. J., Rosin, R. R., and Bell, A. T., *J. Catal.* **134**, 492 (1992).
15. Lietti, L., Forzatti, P., and Bregani, F., *Ind. Eng. Chem. Res.* **35**, 3884 (1996).
16. Casagrande, L., Lietti, L., Nova, I., Forzatti, P., and Baiker, A., *Appl. Catal. B* **22**, 63 (1999).
17. Hermann, J. M., and Disdier, J., *Catal. Today* **56**, 389 (2000).
18. Went, G. T., Oyama, S. T., and Bell, A. T., *J. Phys. Chem.* **94**, 4246 (1990).
19. Ramis, G., Busca, G., Bregani, F., and Forzatti, P., *Appl. Catal.* **64**, 259 (1990).
20. Topsoe, N. Y., *Science* **265**, 1217 (1994).
21. Koebel, M., Madia, G., and Elsener, M., *Catal. Today*, in press.