THE ACTIVITY OF SUPPORTED VANADIUM OXIDE CATALYSTS FOR THE SELECTIVE REDUCTION OF NO WITH AMMONIA

Hans BOSCH[1], Frans J.J.G. JANSSEN[2], Frans M.G. van den KERKHOF[2], Jaap OLDENZIEL[1], Jan G. van OMMEN[1] and Julian R.H. ROSS[1]

1 Twente University of Technology, Dept. of Chem. Techn., P.O. Box 217, 7500AE Enschede, The Netherlands.

2 N.V. KEMA, R&D Division, Dept. Chem. Res., P.O BOX 9035, 6800ET Arnhem, The Netherlands.

ABSTRACT

The activities of monolayer V_2O_5 catalysts for the selective reduction of NO with NH_3 are compared with those of commercial available catalysts containing V and/or W. From steady state and pulse experiments it can be concluded that the reduction of surface sites proceeds either by NH_3 + NO or by NH_3 alone. The re-oxidation of the reduced sites occurs by gaseous oxygen or NO. The experimental reaction stoichiometry can be explained in terms of suitable combinations of these four reactions.

INTRODUCTION

The oxides of nitrogen (NO_x, x = 1/2, 1 or 2) present in stack and flue gases are sources of atmospheric pollution. About 50% of the total burden of NO_x in the USA is emitted by stationary sources [1] and the situation is roughly the same in the Netherlands [2]. Although the amount of so-called "thermal NO_x" (produced directly by the oxidation of nitrogen from the air) can be reduced by to 35% by combustion modification, there will still remain a considerable quant-ity of NO_x which originates from the nitrogen-containing constituents of the fuel [3,4]. Hence, other methods have been introduced for NO_x-removal, notably wet chemical scrubbing and selective catalytic reduction (SCR) [3]; it is gener-ally accepted that the latter is one of the most promising options [5], the reducing agent used so far being exclusively ammonia.

Various catalyst systems have been described in the literature for the SCR reaction [6,7], the most promising of these, particularly from an industrial point of view, being WO_3-TiO_2 [8] and V_2O_5-TiO_2 [9]. A method has been develop-ed in one of our laboratories [10–12] for the preparation of catalysts consist-ing of monolayers of V_2O_5 on TiO_2 or other supports. These materials have relatively high surface areas, good thermal stabilities and also possess good

selective oxidation properties [13]. It is thus of interest to know if these materials will be suitable for use in the SCR of NO_x.

The present paper has two aims. Firstly, it compares the activities for SCR of V_2O_5/TiO_2 monolayer catalysts with those obtained under identical conditions with commercial catalysts containing WO_3 and V_2O_5. Secondly, it compares the results of two types of experiment for studying the reaction over these catalysts: continuous flow and pulse measurements. In the latter type of experiment, we have used a modification of an approach described by Miyamoto et al. [14]. As a result of these measurements, we present a modified and somewhat extended mechanism for the selective reduction of NO_x by NH_3.

EXPERIMENTAL

Catalysts

The main characteristics of the catalysts examined in this paper are given in Table 1. The V_2O_5 used as "bulk oxide" was either as received (Merck "pro analysis") or freshly prepared by calcination of ammonium vanadate at 500^oC. $V_2O_5-TiO_2$ monolayer materials were prepared as described previously [11,12] by adsorption of vanadyl acetylacetonate (Merck "for synthesis")from solution in toluene (Merck, "pro analysis) on a sample of TiO_2 (Degussa) having an area of $50m^2g^{-1}$ and consisting of anatase (68%) and rutile (32%) phases. Wet-impregnated samples were prepared from a solution of ammonium metavanadate in oxalic acid according to the procedure given by Miyamoyo et al. [14]. Two samples of commercially available materials containing WO_3 and a mixture of WO_3 and V_2O_5 supported on TiO_2 (almost pure anatase) were also examined. The V and W contents of all the catalysts were determined using X-ray fluorescence.

Prior to the NO_x reduction experiments, the catalyst samples were calcined in air at 450^oC. The total areas of the freshly calcined materials were obtained using N_2 adsorption with a Carlo Erba Sorptomatic (Type 1800) system controlled by an Apple computer system [15].

Apparatus

The pulse apparatus used was a modified version of that used by Miyamoto et al. [14] and will be described in more detail elsewhere. In essence, it is a system which allows a flow of He over the catalyst to be replaced by a rectangular pulse made up of an identical flow of a mixture of NO and NH_3 in He. The unused reactants and the product water, together with any N_2O formed and a small proportion (<5%) of the nitrogen also produced in the reaction, was trapped in a cold-finger at -195^oC. The remaining nitrogen was then detected with a thermal conductivity detector; alternatively, the mixture could be analysed qualitatively mass-spectrometrically.

A steady-state plug-flow reactor, described in detail elsewhere [16], was used to determine concentration-time relationships, the influence of the oxygen

concentration on the selective reduction reaction and the concentration profiles of NO, NH_3, N_2, H_2O and N_2O. The reactor is coupled by an adjustable leak valve to a mass spectrometer, both the system and the mass spectrometer being operated via an Apple II data system.

All gases used in the pulse experiments were purified by passing them through freshly activated 3X or 4X molecular sieve traps and, where appropriate to remove traces of oxygen, through beds of Cu (BTS). The gases used in the continuous experiments were used without further purification.

Procedures

The pulse experiments were carried out with 100mg of catalyst. The pulse length used was normally 8 min., although other pulse times could be used, and the total gas flow rate was 24 cm^3 min^{-1}. The concentration of NO was kept constant at 2.45% (24500 ppm) and the NH_3 to NO ratio was kept at 1.1. The catalyst temperature was in the range 80° to 400^oC and used samples could be regenerated by heating in air to 450^oC to check reproducibility but a number of experiments were also carried out without this treatment. In some cases, the pulse experiments were stopped immediatly after the initial peak response and the reactor was transferred to equipment for temperature programmed reduction (TPR) experiments [17] where the state of the catalyst was determined using standard TPR techniques using a heating rate of 10^oC min^{-1}.

The steady-state experiments were carried out with 0.1 - 1.68g of catalyst with a total flow of 100 cm^3min^{-1} of a gas mixture 500 ppm of NO, 500 ppm of NH_3 and from 0 - 2% of O_2, the balance being helium. The concentrations of the reactants were thus lower than in the pulse experiments (see below).

RESULTS

Steady-State Experiments

A typical set of results for the concentrations of reactants and products under steady-state operation with a V_2O_5-TiO_2 catalyst are shown in Figure 1 as a function of the catalyst temperature; for clarity, the concentration of oxygen is not shown. Reaction is first evident at a temperature of about 100^oC and the conversion then rises rapidly with temperature until about 250^oC, when conversion of the NO is almost complete; the reaction gives selective production of N_2. The partial pressure of water rises over the whole temperature range. Above about 350^oC, the selectivity decreases as a result of the formation of N_2O; this is due either to the incomplete reduction of the NO with NH_3 or to the direct oxidation of the NH_3. Similar results were found for steady-state operation without oxygen but the activities were lower (see below); in this case also, N_2O was found at higher temperatures.

Figure 2 shows the effect of the concentration of oxygen on the fractional conversion of the NO . It can be seen that there is a very distinct increase in the
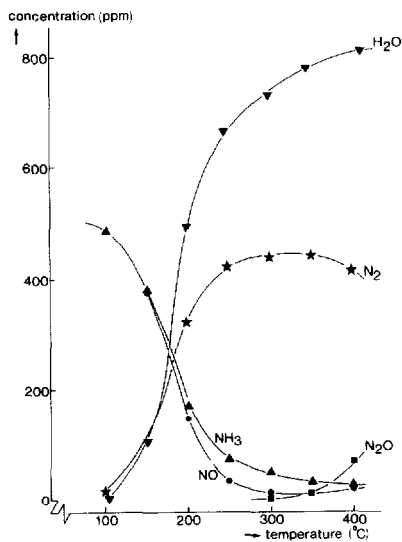
concentration (ppm)

conversion NO

Figure 1 Product distribution in presence of 2% O_2 over 1.9%V/TiO$_2$ as a function of temperature.
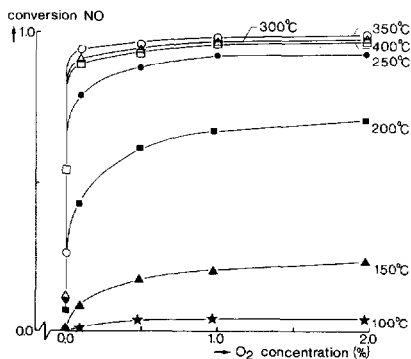
Figure 2 Effect of O_2 concentration on NO conversion over 1.9%V/TiO$_2$ at various temperatures.

conversion at low oxygen concentrations (below 1500 ppm) over the whole temperature range studied, the effect being particularly marked at higher temperatures. The added oxygen takes part in the overall reaction but it is not possible to write a stoichiometric equation for the reaction as the stoichiometry varies with temperature. At temperatures of 350°C and above, all the catalysts examined apart from bulk V_2O_5 were found to give almost complete conversion of the NO in the presence of oxygen.

The activities of the various catalysts were compared for the selective reduction process in the presence of oxygen at the relatively low temperatures of 225° and 250°C are given in Table 1. The three monolayer materials give almost complete (>90%) conversion at 250°C and their performance is better than that of the commercial samples and also of bulk V_2O_5. At 225°C, the conversions are not complete in most cases and so the results at this temperature can be used to make a more quantitative comparison. We assume a simple rate equation of the form:

$$r = k.[NO]^n$$

where n is the order in the NO concentration; we then use the following integrated form to calculate the rate constant, k, assuming plug-flow behaviour:

$$k = \frac{F}{W} \cdot \frac{[NO]_0^{1-n}}{1-n} \cdot \left\{ 1 - (1 - x)^{1-n} \right\} \qquad (1)$$

where F is the volume flow rate $(cm^3 s^{-1})$, W is the sample weight (g), $[NO]_o$ is the NO inlet concentration (ppm) and x is the fraction of NO converted. Wong [18] has reported the value of n to be 2/3 in the temperature range $200^o - 300^oC$ for this reaction and this is supported by our own preliminary measurements [19]. We have thus calculated the rate constants given in Table 1 with a value of n of 0.7. It can be seen from the values given that the sub-monolayer and monolayer catalysts (1.1 to 2.5 wt% V) give the best results. The results for the samples prepared by adsorption are underestimates as the conversion with these samples was almost complete.

It was found for each sample that the steady-state activity in the absence of oxygen was reached only after a period of some 40 to 50 minutes. Typical results are shown in Figure 3. It can be seen that the consumption of ammonia is initially considerably higher than that at the steady state and that the production of water goes through a maximum. In experiments with only NH_3 in the feed, reaction occurred above 300^oC but the rate dropped off rapidly with time; N_2 and H_2O were produced.

Pulse Experiments

The initial effects shown in Figure 3 are seen in a more pronounced way in the results of typical pulse experiments which are shown in Figure 4 for catalyst temperatures of 300° and 375^oC; comparable results are obtained for temperatures as low as 80^oC. All the pulse experiments were carried out without the addition of oxygen to the reaction mixture. In Figure 4, the production of N_2 is plotted as a
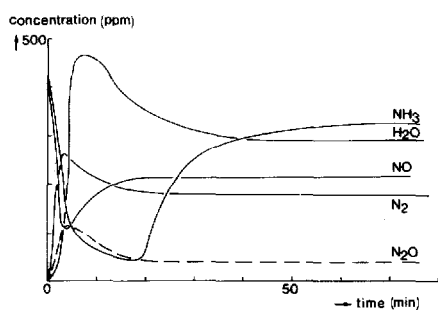

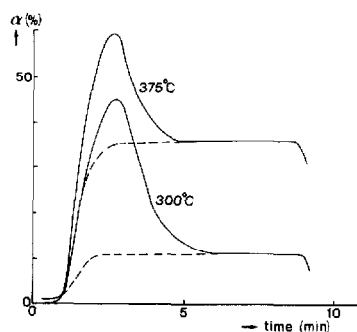Figure 3 Product distribution in the absence of oxygen over 1.9%V/TiO$_2$ at 400°C.

Figure 4 Typical pulse responses: 2.45% NO, NH$_3$/NO = 1.1.

TABLE 1

Steady state activities in the presence of 2% oxygen.

Catalyst	prepn.	V (wt%)	W (wt%)	S_{BET} (m2/g)	weight (g)	225°C conversion (%)	k	250°C conversion (%)
bulk V_2O_5	–	56	–	9	.10	16	18	30
V/TiO_2(D)	a	1.1	–	40	–	–	–	–
V/TiO_2(D)	a	1.8	–	45	.65	98	(40)	98
V/TiO_2(D)	i	1.9	–	45	.10	83	147	93
V/TiO_2(D)	a	2.5	–	45	.60	98	(45)	98
$V/W/TiO_2$	i	2.7	6.5	32	.21	70	17	78
W/TiO_2	i	–	9.9	81	1.68	42	3.4	92

a = adsorption; b = impregnation.

TiO_2 = anatase; TiO_2(D) = anatase (68%) + rutile (32%).

Reaction rate constants calculated from Eq. 1 with n = 0.7.

TABLE 2

Comparison of steady state (ss) and pulse (pu) experiments. No O_2 added.

Catalyst	V (wt%)		weight (g)	300°C conversion (%)	k	350°C conversion (%)	k
bulk V_2O_5	56	ss	.61	8	1.5	47	8
V/TiO_2(D)	1.1	pu	.11	8	6.2	19	15
V/TiO_2(D)	1.8	ss	.65	–	–	60	13
V/TiO_2(D)	1.9	ss	.10	13	15	27	32
		pu	.10	12	11	27	25
V/TiO_2(D)	2.5	ss	.60	–	–	70	18
$V/W/TiO_2$	2.7	ss	.81	30	4.5	48	8
		pu	.10	5	4.3	13	11
W/TiO_2	–	ss	1.60	25	1.9	45	3.7
		pu	.10	5	4.2	9.5	8.2

Reaction rate constants calculated from Eq. 1 with n = 0.7.

function of time for the duration of the NO + NH_3 pulses; the conversion of the NO is plotted, this being calculated on the assumption that one NO molecule reacts to give one N_2 molecule (see below). These results are very similar to those for the N_2 curve of Figure 3, the differences being due to the differences in experimental conditions (space velocities, concentrations and catalyst weight) in the two sets of experiments. According to Miyamoto and his coworkers [14], the N_2 appearing in the first peak is associated with the number of V=O species initially present on the surface of the catalyst and the reaction is summarised by the following equation:

NO + NH_3 + V=O -> N_2 + H_2O + V-OH

where V=O is associated with vanadium present as V^{5+} and V-OH with vanadium in the reduced V^{4+} form.

In order to check these ideas, a series of experiments was carried out to examine the effect of a succession of equivalent pulses at a constant temperature. At $80^{o}C$, the results for consecutive pulses were the same, the initial peaks and the subsequent constant portion not changing from pulse to pulse. However, at temperatures of $300^{o}C$ and above, the initial peak behaviour does not show up in the second and subsequent pulses; only the the activity of the catalyst in the constant part of the curve remains unchanged. Treatment of the catalyst in air between the pulses restores the initial peak response. More significantly, treatment with NO alone of a partly reduced catalyst (reduction either with the reaction mixture or with NH_3 alone above $300^{o}C$, as described above for the continuous flow experiments) also restores the initial peak behaviour; mass spectrometry showed that only N_2 was formed during this treatment.

Temperature programmed reduction (TPR) experiments were carried out with bulk V_2O_5 before and after single pulse experiments of the type shown in Figure 4. The results showed that the TPR behaviour was effectively the same before and after the pulse when the catalyst was held at a temperature of $80^{o}C$; however, after a pulse experiment with the catalyst $350^{o}C$, the TPR profile no longer showed the characteristic two-step reduction from V^{5+} to V^{4+}. We therefore conclude that the second part of the peaks in the pulse experiments corresponds to reaction of NO and ammonia on a surface on which the proportion of V^{5+} sites is greatly reduced. We have used the results to calculate the conversion of NO, x, and hence, using equation 1, values for the rate constant, k, assuming that the same value of n applies in the absence of oxygen. The resultant values of x and k are given in Table 2 together with equivalent data from steady state experiments also carried out in the absence of oxygen. Considering the approximations made and the differences in experimental conditions of the two types of measurements, the results are in remarkably good agreement. They show, as for the experiments in the presence of oxygen (Table 1), that the monolayer materials are more effective than both bulk V_2O_5 and the commercial materials.

DISCUSSION

One of the important issues in the selective catalytic reduction of the oxides of nitrogen is the nature of the active site or sites. The present results throw further light on the subject.

In the model of Miyamoto and his coworkers [14], it is proposed that only V^{5+} in the form of V=O groups acts as an active site. After adsorption of NH_3 and the subsequent reaction with gaseous NO, reduced V^{4+} in the form of V-OH groups is left behind:

$$V=O + NH_3 + NO \rightarrow V-OH + N_2 + H_2O \qquad (2a)$$
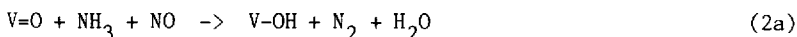
Gaseous O_2 or oxygen from the underlying layers of the active phase is then used to reoxidise these sites:

$$2V-OH + [O] \rightarrow 2V=O + H_2O \qquad (2b)$$

The activity is determined by the concentration of the V=O active sites which is at a maximum either in the presence of oxygen or on a freshly calcined catalyst. The model is thus compatible with the large effect of oxygen pressure on the rate of reaction (Figure 2) and the high initial activity in the absence of oxygen (Figure 3). Also, from TPR results, it is known that bulk V_2O_5 requires higher temperatures for reduction than does V_2O_5 in a monolayer; on going from a monolayer to supported crystals of V_2O_5, the temperature of reduction gradually increases [20]. One can therefore understand the higher activity for the NO_x reduction reaction of the monolayer materials when compared with bulk V_2O_5. The lower activity of samples containing WO_3 can also be explained, as supported WO_3 is more difficult to reduce than is supported V_2O_5. With monolayer materials, the influence of support is clearly very important. These conclusions fit in well with the surface structure put forward by Bond et al. [20] in which the oxygen is bonded more loosely to vanadium in a monolayer. Similar effects have previously been reported for oxidation reactions [13].
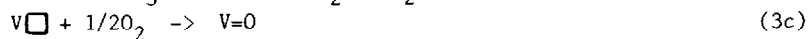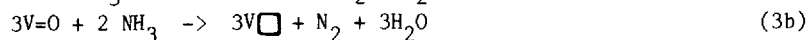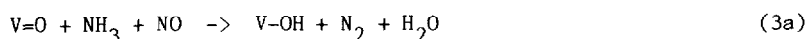
Not all the observations made in the present work can be explained by the sequence of reactions given in equations 2a and b: (i) at temperatures of $300^{\circ}C$ and above in the absence of NO, NH_3 reacts with the catalyst to give N_2 and H_2O; (ii) a catalyst reduced either by NO + NH_3 mixtures or by NH_3 alone (see Pulse Experiments) can be regenerated by NO alone with the production of N_2; (iii) the constant steady-state activities in the absence of oxygen can be maintained for hours; and (iv) the catalyst is not regenerated by oxygen from underlying layers of the catalyst between pulses in the pulse experiments at higher temperatures as no initial peak is observed in subsequent pulses.

In the case of the monolayer catalysts, it is not possible to reoxidise reduced surface sites by oxygen from the bulk as in step 2b. Furthermore, if there was oxygen available for reoxidation from the underlying layers and the model of equation 2 held, the rate of the reaction is likely to determined by step 2b which is essentially diffusion controlled. The catalyst would be exhausted rapidly if no gaseous oxygen was present. For the experimental conditions of Figure 3 and for the

reaction rate observed, it can be calculated that the catalyst would be exhausted in 15 minutes if oxygen from the bulk was used, and this is clearly not the case. As the pulses used in the experiments of Miyamoto et al. lasted only one minute [14], exhaustion of the underlying layers would not have been expected.

We therefore conclude that that step 2b above does not play an important role in the all-over reaction. Instead, we suggest that the reduced surface sites can also exhibit significant activities at temperatures of $300^{\circ}C$ and above. All the observations can be accounted for by the following scheme in which reduction of surface sites can occur in step 3a and b and reoxidation by steps 3c and d:

$$V=O + NH_3 + NO \rightarrow V-OH + N_2 + H_2O \qquad (3a)$$
$$3V=O + 2 NH_3 \rightarrow 3V\square + N_2 + 3H_2O \qquad (3b)$$
$$V\square + 1/2O_2 \rightarrow V=O \qquad (3c)$$
$$V\square + NO \rightarrow V=O + 1/2 N_2 \qquad (3d)$$

In steps 3c and d, $V\square$ can represent either a V-OH group (as in the model of Miyamoto et al [14]) or a surface vacancy. Steps 3a and b are in competition as are steps 3c and d if O_2 is present. The scheme shows that neither oxygen from the underlying layers nor oxygen from the gas phase is essential for the reduction of NO with NH_3 to give N_2.

It is possible to use a combination of equations 3a to d to explain the experimentally observed variation of the all-over stoichiometry of the reaction with reaction conditions. In the presence of oxygen and at low temperatures, equations 3a and c can be combined to give:

$$O_2 + 4NH_3 + 4NO \rightarrow 4N_2 + 6H_2O \qquad (4a)$$
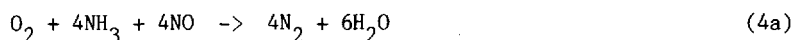
while in the absence of O_2, also at low temperatures, a combination of equations 3a and d give:

$$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O \qquad (4b)$$

Equation 3b also plays a role which becomes more significant at higher temperatures and so the reaction stoichiometries both with and without oxygen change apprecibly with temperature.

Preliminary measurements with labelled oxygen carried out with the monolayer catalysts in the continuous flow equipment [19] give additional support for the extended mechanism which we put forward above. Further experiments are in progress.

CONCLUSIONS

1. The results of stationary state and pulse experiments are in good agreement.
2. Oxygen has a large influence on the reaction rate, possibly due to the re-occupation by the oxygen of surface vacancies.
3. Monolayer catalysts show better activities at similar V loadings than those of commercial catalysts containing V and/or W due to the greater ease of reduction of the monolayer materials.
4. At least two types of active site play a role in the selective reduction of NO; these are probably due to the presence of vanadium with valency of both +4 and +5.

5. Two different reactions occur on these different sites, the proportions of which depend on the reaction conditions.

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