

Mechanism of the Reaction of Nitric Oxide, Ammonia, and Oxygen over Vanadia Catalysts. 2. Isotopic Transient Studies with Oxygen-18 and Nitrogen-15†

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The mechanism of nitric oxide reduction with ammonia to form N_2 , H_2O , and N_2O both in the presence and in the absence of O_2 over the following series of catalysts, unsupported V_2O_5 , V_2O_5 on TiO_2 , V_2O_5 on SiO_2/Al_2O_3 , and V_2O_5 on Al_2O_3 , has been investigated with the aid of labeled O_2 and labeled NH_3 at 400 °C. The behavior of ammonia was studied both in the presence and in the absence of O_2 . The presence of labeled O_2 gives extra information about the product distribution and the reaction mechanism. Evidence is given that ammonia does not react with O_2 or O from any source during the reaction, but that nitrogen and nitrous oxide were produced by a reaction involving all three species, NO , NH_3 , and/or O_2 . Nitrous oxide and water are both formed at two different sites of the catalyst. A series of transient tracing studies were performed in a plug-flow reactor using $^{15}NH_3$ and $^{18}O_2$. Both ^{15}NN and ^{15}NNO were produced on the unsupported V_2O_5 , V_2O_5 on TiO_2 , V_2O_5 on SiO_2/Al_2O_3 , and V_2O_5 on Al_2O_3 with very high selectivities. The mechanism of the reaction of NO , NH_3 , and O_2 , proposed in a previous paper (ref 2), is further evaluated on the basis of this new experimental evidence.

Introduction

It was found in a previous study by Bosch et al.¹ that the steady state of the reduction of NO by NH_3 to form N_2 and H_2O is reached only after about 50 min in the absence of oxygen over a V_2O_5 on TiO_2 catalyst. Moreover, during this induction period the consumption of ammonia was considerably higher than that in the steady state and the production of water went through a maximum. Furthermore, it was concluded for monolayer catalysts that oxygen from the underlying layers does not play an important role in the overall reaction. In situ temperature-programmed reduction measurements with hydrogen¹ showed that the surface of the catalyst had been reduced after the reduction of NO with NH_3 had been carried out.

In the preceding study,² we described the role of oxygen in the selective catalytic reduction of nitric oxide with ammonia. It was assumed there that both the chemisorbed ammonia species and the physisorbed ammonia species are able to react with nitric oxide via an Eley-Rideal mechanism. Chemisorbed ammonia species are defined here as being nitrogen-hydrogen-containing species present on the surface during the reaction at 400 °C. Physisorbed ammonia species are the result of the reaction of OH groups present on the surface with NH_3 . Two "types" of water are formed: that originating from the reaction of gaseous NO with the chemisorbed ammonia species and that formed as a result of the dehydration of OH groups present on the surface of the catalyst. Thus, lattice oxygen shared with adjacent sites was involved in the reaction. Furthermore, it was shown that gaseous oxygen could be exchanged with the lattice oxygen of the catalyst during reaction in the temperature region of 300–400 °C. Scrambling of NO with $V=O$ groups was also observed. However, the role of ammonia and of nitric oxide in the formation of N_2O was not clear and only a suggestion of the mechanism was given. The behavior of ammonia during the reaction and its ability to reduce the surface of the catalyst before the reaction can give valuable information about the reaction mechanism. The present paper thus describes an investigation of the mechanism of the reduction of NO with $^{15}NH_3$ or $^{14}NH_3$ in the presence of $^{16}O_2$ or $^{18}O_2$ at concentration levels of about 500 ppm using a plug-flow reactor; the catalysts used were unsupported V_2O_5 , V_2O_5 on TiO_2 , V_2O_5 on Al_2O_3 , and V_2O_5 on SiO_2/Al_2O_3 catalysts. From the measured product distributions, it was possible to deduce reaction

TABLE I: Catalysts Used in This Study²

no.	catalyst	vanadium content, %	S_{BET} , m ² /g	particle size, mm
1	V_2O_5/TiO_2	1.9	45	0.3–0.6
2	$V_2O_5/SiO_2/Al_2O_3$	5.6	140	0.25–0.5
3	V_2O_5/Al_2O_3	8	170	0.25–0.5
4	V_2O_5/Al_2O_3	4.4	207	0.25–0.5
5	V_2O_5	58	10.5	0.25–0.5

paths. All the catalysts were studied at 400 °C, at which temperature nitrous oxide is produced; observations made on the production of the nitrous oxide contribute to a better understanding of the mechanism of the overall reaction. The effect of ammonia on the catalysts in the absence of nitric oxide and oxygen was also studied. The results are used to give further support for a mechanism proposed previously.²

Experimental Section

Catalysts. The catalysts used in this study and their main characteristics are summarized in Table I. Other experimental details are described in the preceding paper.² Prior to the NO reduction experiments, the catalyst samples were calcined in situ with helium containing 25% oxygen at 300–400 °C.

Gases. $^{15}NH_3$ and $^{18}O_2$ (isotopic purity 99 atom %) were obtained from MSD isotopes (Canada) and were used without further purification. Gas mixtures of $^{15}NH_3$, O_2 , and $^{18}O_2$ with helium up to 10 MPa with concentrations of about 1000–2000 ppm were prepared by conventional static gravimetric methods in our laboratory. Various mixtures of NO , NH_3 , and O_2 were established with the aid of mass flow controllers (Matheson). It was not possible to carry out experiments in the complete absence of oxygen as trace quantities (1–5 ppm) were always present in the different gas streams. Thus, the description in the text "in the absence of oxygen" means that there was no oxygen added to the gas mixture. Mass spectrometric peaks were examined up m/e 48 ($^{15}N_2^{18}O$). The masses of $^{15}NH_3$, m/e 18 and $^{15}N_2$, m/e 30 coincide with those of H_2O and NO and the quantities of these species were therefore determined from the nitrogen material

(1) Bosch, H.; Janssen, F.; van den Kerkhof, F.; Oldenzil, J.; van Ommen, J. G.; Ross, J. R. H. *Appl. Catal.* **1986**, *25*, 239.

(2) Janssen, F. J. J. G.; van den Kerkhof, F. M. G.; Bosch, H.; Ross, J. R. H. *J. Phys. Chem.*, in press.

† For part 1, see ref 2.

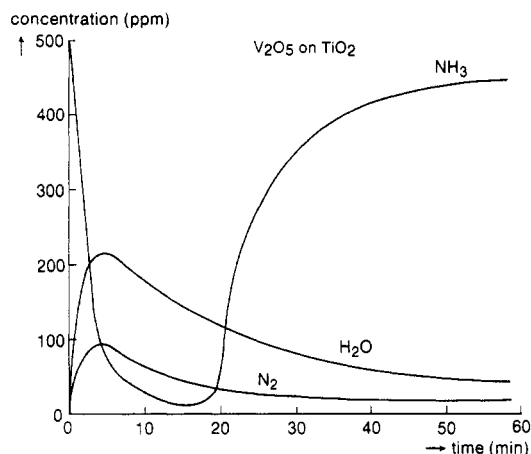


Figure 1. The reaction of ammonia with the V_2O_5 on TiO_2 catalyst at $400\text{ }^\circ\text{C}$. $[NH_3]_i = 500\text{ ppm}$, 100 mg of catalyst, balance helium.

balance and the results of reactions carried out without tracers.

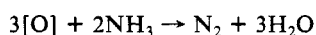
Apparatus and Procedures. The apparatus used and the procedures adopted are essentially those described previously.² During the calibration of the mass spectrometer with known mixtures of NO , NH_3 , and O_2 , helium was passed over the catalyst. After the calibration, the eight-port valve (shown in Figure 1 of ref 2) was switched and the helium stream was replaced by the calibration mixture. There is thus always a deviation in the response caused by flushing helium from the reactor (see Results).

Three distinct types of experiments have been carried out: (1) after the reduction of the catalyst with ammonia at $400\text{ }^\circ\text{C}$, NO was introduced on the catalyst and the resulting reaction products were measured by the mass spectrometer; (2) the same type of experiment was repeated with a prereduced catalyst, admitting a mixture of NO and NH_3 ; and (3) as in (2) but with a $NO/NH_3/O_2$ mixture. Various combinations of labeled molecules were used and experiments were also carried out in which the isotopic composition was changed in step functions.

Results and Interpretation

Three types of experiments have been carried out on the catalysts V_2O_5 on TiO_2 and V_2O_5 on Al_2O_3 which were previously reduced by NH_3 or $^{15}NH_3$ at $400\text{ }^\circ\text{C}$. In the first type of experiment the prereduced catalyst sample was flushed with helium in order to remove physisorbed ammonia from the walls of the tubing and other parts of the experimental system, and then exposed to NO . In the second type, the reaction of NO with NH_3 was examined over the reduced catalyst, while in the third type, O_2 was added to the NO and NH_3 reaction mixture, again over the reduced catalyst.

Reduction of the Catalysts with NH_3 . Figure 1 shows the concentration profiles for the compounds NH_3 , N_2 , and H_2O obtained during the reduction with ammonia of the catalyst V_2O_5 on TiO_2 . After 20 min, during which time all the ammonia was used, ammonia appeared in the effluent stream; however, the reaction was still not complete even after 60 min. Ammonia was thus oxidized by the catalyst surface, resulting in the products nitrogen and water. The curves of water and nitrogen were graphically integrated between 0 and 60 min and the ratio of the amounts of water and nitrogen was found to be about 3 and is in agreement with the stoichiometry



where $[O]$ represents the amount of oxygen available from the catalyst. For this experiment, $[O]$ was about $25\text{ }\mu\text{mol}$ of oxygen, and this quantity can be compared with $93\text{ }\mu\text{mol}$ of oxygen present in the V_2O_5 part of the catalyst. Hence one of the five oxygen atoms of each V_2O_5 species is removed, assuming that the V_2O_5 is present on the catalyst surface, that the TiO_2 does not take part in the oxidation of the ammonia, and that oxygen removal is uniform across the surface of the catalyst. From the measured amounts of water and nitrogen, it could also be calculated that

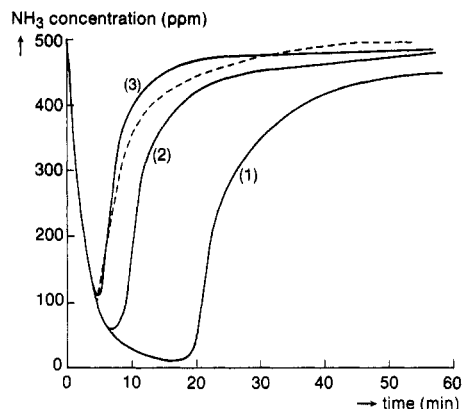


Figure 2. Concentration profiles of ammonia as a function of time on the (50 mg) V_2O_5 on TiO_2 catalyst at $400\text{ }^\circ\text{C}$. The experiments were carried out successively. Curve 1: Concentration profile of ammonia on a freshly calcined catalyst (1 h oxygen at $300\text{ }^\circ\text{C}$). Curve 2: The profile after the catalyst was flushed with helium during one hour at $400\text{ }^\circ\text{C}$. Curve 3 is determined after the catalyst was flushed with helium for 10 h at $400\text{ }^\circ\text{C}$. The dotted line is the breakthrough curve of ammonia for an empty reactor.

the consumption of NH_3 by the catalyst was about 0.4 mol of NH_3 per mole of V.

After the catalyst was flushed with helium at $400\text{ }^\circ\text{C}$ for 1 h, ammonia was reintroduced. Further reaction occurred; the consumption of NH_3 is shown by curve 2 of Figure 2, where it is compared with the equivalent curve for the fresh catalyst (curve 1, taken from Figure 1). When this procedure was repeated, with the difference that the catalyst was now flushed for 10 h with helium, the results of curve 3 were obtained. Curve 3 fits roughly on the breakthrough curve (dotted line) obtained when ammonia was fed to the empty reactor, indicating that no further reaction occurred in the experiment of curve 3 and that the catalyst had become inactive further the reduction by NH_3 . These results were confirmed by thermogravimetric measurements, which indicated that the catalyst could be reduced by ammonia to $V(IV)$. From the ammonia profiles of Figure 1 and 2, it was not possible to calculate the amount of ammonia left behind on the surface of the catalyst.

The Reaction of NO with the Prereduced Catalyst. In the following three types of experiments the catalysts V_2O_5 on Al_2O_3 (no. 4) and V_2O_5 on TiO_2 were reduced with $^{15}NH_3$ at $400\text{ }^\circ\text{C}$. $^{15}NH_3$ was used instead of NH_3 in order to distinguish between the nitrogen compounds which occur from subsequent reaction of NO with adsorbed nitrogen species or with the surface of the catalyst. The number of moles of NH_3 consumed per mole of V by the catalysts V_2O_5 on Al_2O_3 (no. 4) and V_2O_5 on TiO_2 were found to be 0.16 and 0.40, respectively. These values were corrected for the number of micromoles of NH_3 which reacted with gaseous oxygen already present in the gas mixtures. After the reduction, the catalysts were flushed with helium at $400\text{ }^\circ\text{C}$ (1 or 3 h). NO was then introduced, and this was found to reoxidize the catalyst, giving N_2 as predominant product. During this reaction on the catalyst V_2O_5 on Al_2O_3 (no. 4), ^{15}NN , ^{15}NNO , H_2O , and O_2 were also found in the exhaust gas. From the quantity of ^{15}NN found in this experiment it can be calculated that about 20% of the ammonia reacted was still present as a ^{15}N -containing species on the prereduced catalyst before the reaction. These species disappeared when the catalyst was heated in helium at $400\text{ }^\circ\text{C}$ for prolonged times. This was also found to be the case for a similar experiment on the V_2O_5 on TiO_2 catalyst; with this only small amounts of N_2 (10^{-9} mol) and N_2O (10^{-10} mol) were found.

The Reaction of NO and NH_3 with the Prereduced Catalyst. To study the effect of the reduced surface on the reaction of NO and NH_3 , the catalyst V_2O_5 on TiO_2 (no. 1, Table I) was reduced with NH_3 at $400\text{ }^\circ\text{C}$ for 13 h. After the reduction, a mixture of NO and NH_3 was introduced to the catalyst and the products nitrogen, nitrous oxide, and water were formed. As is shown in Figure 3, a high initial activity in the absence of oxygen was

TABLE II: Distribution of the Nitrogen-Containing Products of the Reaction of Nitric Oxide, Ammonia, and Oxygen at the Steady State during Transient Tracer Experiments^a

	catalyst (no.)															
	V ₂ O ₅ /TiO ₂ (1)			V ₂ O ₅ /SiO ₂ /Al ₂ O ₃ (2)			V ₂ O ₅ /Al ₂ O ₃ (3)			V ₂ O ₅ /Al ₂ O ₃ (4)			V ₂ O ₅ (5)			
	I	II ^b	III	I	II	III	I	II	III	I	II	III	I	II	III	
time, c min	280	300	500	300	500	700	300	500	700	300	500	700	300	500	700	
(m/e)	(species)															
28	N ₂	73.9	43.4	2.5	78.3	7.6	5.5	85.4	14.8	4.2	81.4	14.6	0.8	29.0	12.4	6.3
29	¹⁵ NN	0	34.9	73.0	0	73.3	86.9	0	72.8	92.3	0	71.7	95.4	0	20.7	27.9
32	N ¹⁸ O	4.5	4.8	0	14.4	14.0	0	11.6	10.6	0	14.2	11.6	0	23.7	22.8	0
44	N ₂ O	14.9	7.3	1.7	6.1	0.3	0	1.7	0	0.4	4.4	0.3	0.4	32.0	1.7	1.9
46	N ₂ ¹⁸ O	6.7	2.5	0	1.3	0	0	0.3	0	0	0	0	0	15.3	1.9	2.7
45	¹⁵ NNO	0	5.7	22.8	0	4.9	7.6	0	1.8	3.1	0	1.7	3.4	0	27.8	61.2
47	¹⁵ NN ¹⁸ O	0	1.4	0	0	0	0	0	0	0	0	0	0	0	12.7	0
18	H ₂ O, ppm	432	500	578	341	341	482	459	445	486	309	285	350	365	325	500
20	H ₂ ¹⁸ O, ppm	263	236	6	111	111	21	100	89	21	70	70	2	229	234	18
conversion, %		85	81	78	53	51	52	51	50	55	56	56	57	33	29	36
selectivity		0.76		0.76	0.84		0.92	0.91		0.97	0.88		0.97	0.33		0.31
H ₂ O/H ₂ ¹⁸ O		1.6	2.1		3.1	3.1		4.6	5.0		4.4	4.1		1.2	1.4	

^a The concentrations are relative concentrations with respect to the total concentration of the nitrogen compounds mentioned in the table. The compositions of the starting gas mixtures are as follows: part I, [NO]_i = [NH₃]_i = 500 ppm; [¹⁸O₂]_i = 581 ppm; part II, [NO]_i = 500 ppm; [¹⁵NH₃]_i = 473 ppm; [¹⁸O₂]_i = 581 ppm; part III, [NO]_i = 500 ppm; [¹⁵NH₃]_i = 473 ppm; [O₂]_i = 495 ppm. In all parts of the experiments, the balance gas was helium. The conversion is expressed as the amount of the N₂ formed relative to the [NO]_i. The selectivity is defined as 2[N₂]/Σ[N] for part I and [¹⁵NN]/Σ[¹⁵N] for part III. ^b The figures of part II for the V₂O₅ on TiO₂ catalyst were taken at 20 min. With respect to the isotopic composition, the catalyst was not at steady state. ^c Time after which the steady state was attained and also at which the figures were taken.

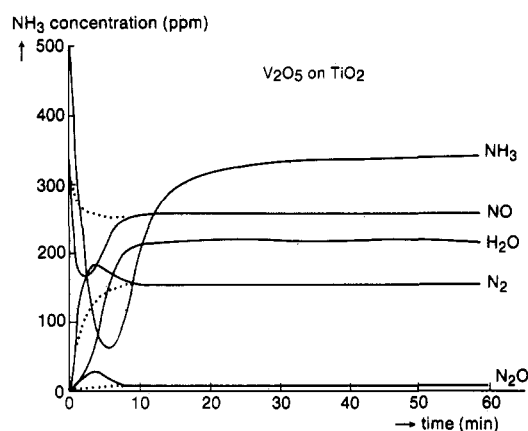
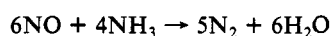
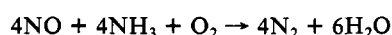


Figure 3. Concentration profiles as a function of time for the products NH₃, NO, H₂O, N₂, and N₂O of the reaction of NO and NH₃ at 400 °C on the V₂O₅ on TiO₂ catalyst, after the catalyst was treated with NH₃ in helium for 13 h at 400 °C (see also Figure 2). [NO]_i = [NH₃]_i = 500 ppm, balance helium.

observed when a mixture of NO and NH₃ was admitted to the catalyst at 400 °C. Extra NO was thus consumed and extra N₂ and some N₂O were produced initially. The steady-state concentration of NO was lower than that of the NH₃ concentration, because NO was needed to reoxidize the oxygen vacancies. According to the material balance, the predominant overall reaction to occur is



The integrated area of the "overshoot peak" of NO, the area between the full and the dotted curve for NO in Figure 3, is roughly equal to the sum of the integrated areas of the equivalent overshoot peaks of N₂O and N₂. The phenomenon of the overshoot of NO, N₂, and N₂O appears to arise from the reaction of the NO with nitrogen-containing species already present at the surface as a result of the reduction. The water profile shows no overshoot, as can be seen in Figure 3, and we thus conclude that there is no oxygen available on the surface after the reaction with ammonia for the overall reaction:



Such a reaction was found when a calcined catalyst was used.¹ Similar experiments were carried out with a mixture of NO and

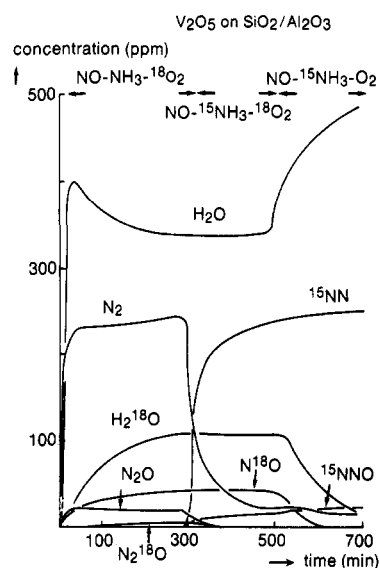


Figure 4. Concentration profiles as a function of time for H₂O, N₂, H₂¹⁸O, N¹⁸O, N₂O, ¹⁵NN, and ¹⁵NNO over the catalyst V₂O₅ on SiO₂/Al₂O₃. In the period 0–290 min, the incoming gas composition is 500 ppm NO; 500 ppm NH₃; 581 ppm ¹⁸O₂. In the periods 290–490 min and 490–690 min, the initial concentrations were 500 ppm NO, 473 ppm ¹⁵NH₃, 581 ppm ¹⁸O₂; and 500 ppm NO, 473 ppm ¹⁵NH₃, 495 ppm O₂, respectively. Temperature 400 °C; balance helium (see also Table I).

¹⁵NH₃ on the samples of V₂O₅ on Al₂O₃ (no. 4) and the V₂O₅ on TiO₂ catalysts after reduction with ¹⁵NH₃ (Table II). In these cases the reaction products were found to be ¹⁵NN, ¹⁵NNO, and H₂O. The products N₂ and N₂O were thus produced exclusively from equimolar quantities of NO and NH₃. Minor quantities (about 10⁻⁹ mol) of N₂O and N₂ were also observed during the reaction which suggests that there is some interaction of NO with the surface of the catalyst. However, when oxygen was added to the gas mixtures, no N₂ or N₂O was formed.

The Reaction of NO, NH₃, and O₂ over the Prereduced Catalysts. Figure 4 gives an example the results of transient measurements of the selective catalytic reduction of NO with NH₃ at 400 °C in the presence of oxygen on the catalyst V₂O₅ on SiO₂/Al₂O₃. During the experiments, which can be divided into three parts, the concentrations of the components were abruptly changed in the following sequence: part I, NO, NH₃, ¹⁸O₂; part

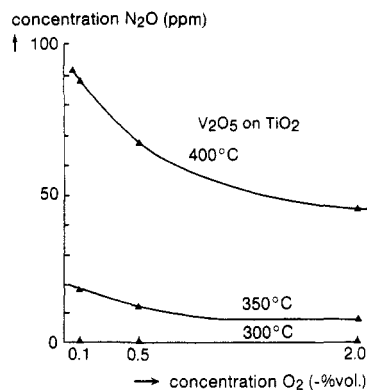


Figure 5. N_2O concentration as a function of oxygen concentration at three temperatures on the catalyst V_2O_5 on TiO_2 . $[\text{NO}]_i = [\text{NH}_3]_i = 500$ ppm, balance helium.

II, NO , $^{15}\text{NH}_3$, $^{18}\text{O}_2$; part III, NO , $^{15}\text{NH}_3$, O_2 . Because of the inequality of the concentrations of $^{18}\text{O}_2$ and $^{16}\text{O}_2$ and of $^{15}\text{NH}_3$ and NH_3 , the conversions of NO are not the same in the three parts (Table I). As already mentioned in the preceding paper,² the H_2^{18}O concentration increases as the H_2O concentration decreases. When NH_3 in the feed was replaced after about 300 min by $^{15}\text{NH}_3$ (Figure 4), the N_2O and N_2^{18}O of the product stream were replaced completely by the respective isotopic nitrous oxide isomers, ^{15}NNO and $^{15}\text{NN}^{18}\text{O}$. The oxygen atom in ^{15}NNO remained attached to a nitrogen atom with which it was associated in the NO molecule. $^{15}\text{NN}^{18}\text{O}$ is thus probably coming from a scrambling of ^{15}NNO with a catalyst surface containing oxygen-18. No formation of $^{15}\text{N}_2\text{O}$ or $^{15}\text{N}_2^{18}\text{O}$ has been found with any of the catalysts and this means that the $^{15}\text{NH}_3$ was not oxidized to $^{15}\text{N}_2\text{O}$ over the catalyst. Table II summarizes the concentration of a number of the compounds found during the transient studies of the type described above on the five catalysts examined. With respect to N_2O formation, all the catalysts showed the same behavior. The phenomena which appeared in the different parts of the experiments can be described as follows. Part I for each catalyst gives the concentration of some of the products of the reaction of NO , NH_3 , and $^{18}\text{O}_2$. On all the catalysts, N^{18}O , N_2 , H_2^{18}O and N_2O were formed. N_2^{18}O was only found in large amounts on unsupported V_2O_5 and on V_2O_5 on TiO_2 . In part II (NH_3 is switched to $^{15}\text{NH}_3$) of the experiments summarized in Table II the same compounds as in part I were formed, in addition to ^{15}NN and ^{15}NNO . On two of the catalysts, V_2O_5 and V_2O_5 on TiO_2 , N_2^{18}O and $^{15}\text{NN}^{18}\text{O}$ were also formed. The change of concentration of ammonia did not occur as an ideal step function, because of the presence in the system of adsorbed NH_3 . All the values presented in Table II were taken at steady state; except for those of part II of the V_2O_5 on TiO_2 catalyst these values were taken at 20 min. In part III, the reaction of NO , $^{15}\text{NH}_3$, and O_2 gave predominantly the compounds ^{15}NN and ^{15}NNO and to a lesser extent N_2 and N_2O . The mass spectrometer is able to distinguish between N^{15}NO and ^{15}NNO .³ These compounds show fragment ions at m/e 31 and m/e 30, respectively; it was established that no N^{15}NO was formed. On the other catalysts, only N^{18}O (m/e 32), N_2O (m/e 44), and ^{15}NNO (m/e 45) were formed. The selectivities of ^{15}NN relative to that of ^{15}NNO (defined as $([^{15}\text{NN}])/([^{15}\text{NN}] + [^{15}\text{NNO}])$) for the reaction of NO , $^{15}\text{NH}_3$, and O_2 for the catalysts 1–5 (Table I part III) were 0.76, 0.92, 0.98, and 0.31. From these results, it appears that if the specific surface area of the catalyst increases, the selectivity to ^{15}NN also increases. It is shown in Figure 5 for the catalyst V_2O_5 on TiO_2 , that the amount of N_2O formed depends on the gaseous oxygen concentration; as the oxygen concentration decreases, the nitrous oxide concentration increases.

The best fit of the curve of Figure 5 was found to be a logarithmic function of the form

$$[\text{N}_2\text{O}] = 55.4 - 13.1 \ln [\text{O}_2]$$

in the oxygen concentration range 0.05–2 vol % O_2 . The dependence of N_2O on the oxygen concentration was less marked

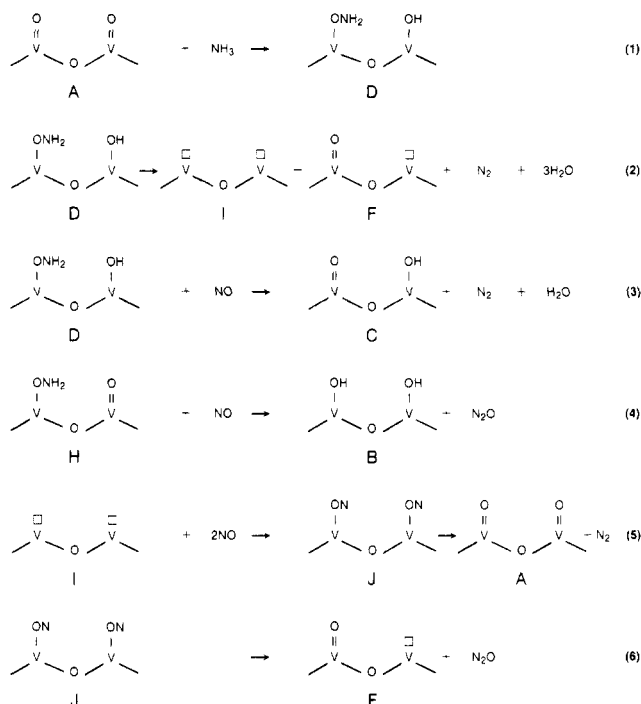


Figure 6. Proposed sequence of reactions for the reduction of NO by NH_3 over a supported vanadia catalyst to form N_2 , H_2O , and N_2O . Reactions 1 and 3 were discussed in a previous paper.² For the nomenclature of the various species the same symbols are used as in ref. 2.

at lower temperatures. ^{15}NN and ^{15}NNO were formed on the catalysts (part III, Table II); no reaction occurs in the absence of catalyst. $^{15}\text{N}_2$ (m/e 30) is likely to be formed but could not be detected in the experiments because its mass coincides with the mass of nitric oxide. Preliminary experiments with mixtures of ^{15}NO , NH_3 , and O_2 over the unsupported V_2O_5 and V_2O_5 on TiO_2 catalysts have shown that $^{15}\text{N}_2$ could be produced in relatively large amounts: about 6% of the total amount of nitrogen formed. From Table II, it follows that NO shows interaction with the labeled catalyst surface, because of the formation of N^{18}O (m/e 32). However, no $^{15}\text{N}^{18}\text{O}$, a possible reaction product of $^{15}\text{NH}_3$ with the surface oxygen, was found.

Discussion

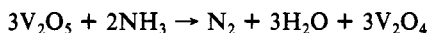
As was discussed in the preceding paper,² three important items are involved in a series of reactions NO , NH_3 , and O_2 . First, the formation of water occurs both by a dehydration step and by an Eley-Rideal mechanism. Second, the formation of nitrogen, which is produced from nitric oxide and ammonia, occurs via an Eley-Rideal mechanism. Third, nitrous oxide is also formed out of one molecule of nitric oxide and one molecule of ammonia. The formation of water was discussed in detail in the preceding paper.² A number of reactions are added to those previously presented to explain the formation of nitrous oxide. The most important reactions are summarized in Figure 6. These reaction sequences help us to explain our ideas about the reaction mechanism. For the nomenclature of the various species the same symbols are used as in the preceding paper.²

The Interaction of NH_3 with the Oxidic Surface. We postulate that ammonia chemisorbs on the surface at 400 °C according to reaction 1 shown in Figure 6 resulting in a nitrogen-containing species and an OH group. The presence of an NH_2 species on the surface has been suggested by several authors.²⁻⁴ The arrangement of atoms such as $\text{V}-\text{ONH}_2$ was chosen because of the hypothesis that $\text{V}-\text{ONH}_2$ could be formed from the reaction of NH_2OH and a hydroxyl group on the surface of the oxide. However, we have no experimental evidence or proof of its presence yet.

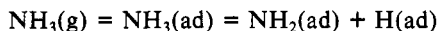
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Subsequent reaction of this dissociated ammonia species in the presence of NO does not lead to the oxidation preadsorbed ¹⁵N-containing species, because no ¹⁵N₂, ¹⁵NO, ¹⁵N¹⁸O, ¹⁵N₂O, or ¹⁵N₂¹⁸O was found on the V₂O₅ on Al₂O₃ and V₂O₅ on SiO₂/Al₂O₃ catalysts (Table II). On the V₂O₅ and V₂O₅ on TiO₂ catalysts, oxidation of ¹⁵NH₃ to ¹⁵N₂ was able to occur. It is suggested here that chemisorbed ammonia in the absence of NO leads to the oxidation/dehydration of the surface species D forming species F and I (reaction 2). At 400 °C, NH₃ is thus oxidized and V(V) is reduced to V(IV) according to the overall stoichiometry



Ammonia is selectively oxidized to N₂ and H₂O and not to N₂O. From the amounts of ammonia reacted (see Results and Interpretation) it can be calculated that 0.24 and 0.12 molecules ammonia per vanadium atom were consumed for the V₂O₅ on TiO₂ (no. 1) and V₂O₅ on Al₂O₃ (no. 4) catalysts, respectively, and that the calculated number of oxygen removed per vanadium atom were 0.36 and 0.18, respectively. In the previous paper,² it was calculated that up to a maximum of half of the surface area could be covered by OH groups during the reaction of NO, NH₃, and O₂. This implies also that a maximum of half of the adsorption sites could be occupied by NH₃ species. In the experiments on the reduction of the catalysts with ammonia, this proportion is lower because of the formation of molecular nitrogen from two adjacent nitrogen atoms. This can be explained by suggesting that a nitrogen atom present on the oxide surface must become paired with another N atom present on the surface so that recombination into an N₂ molecule and desorption of it may occur. However, in order that nitrogen atoms can be adsorbed and subsequently combine with one another an uninterrupted layer of oxygen atoms is necessary. During the reduction, the number of oxygen vacancies increases and these are not refilled by oxygen atoms as is the case when oxygen or nitric oxide is present in the gas phase. Another important point is that two adjacent lattice oxygen atoms are needed for the chemisorption of an NH₃ species and an H atom (species A in Figure 6):



(NH₂)ad can then react further on the surface, according to the equation

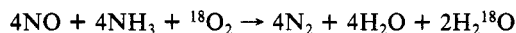


It was found by reaction of NO with the prereduced catalyst that 20% of the ammonia used for reduction still remained as nitrogen-containing species on the surface after 1 h of reduction and a further hour of flushing the catalyst with helium. The nitrogen-containing species disappeared when the catalyst was heated in helium for more than 3 h. The helium used contained traces of oxygen and this probably restored the oxygen vacancies on the surfaces and thus permitted the nitrogen atoms to combine to give N₂. Haber et al.⁵ used hydrogen to reduce a monolayer V₂O₅ on TiO₂ (anatase) catalyst at 400 °C and found one oxygen atom was removed for each vanadium polyhedron and that the number of oxygen atoms which can be removed from each VO₄ polyhedron is independent of the nature of the reducing agent (H₂, CO, or hydrocarbons). However, in our case, reducing the catalyst with ammonia results in removal of about one oxygen atom per two vanadium atoms. After reducing the catalyst with ammonia and then flushing the reduced material for 3 h and introducing NO, or NO and NH₃, it was suggested in our previous paper² that N₂ and N₂O were formed by an Eley-Rideal mechanism (reactions 3 and 4 in Figure 6).

It was found in this work and in the previous paper² that whether or not oxygen was used, most of the nitrogen (N₂) as well as the nitrous oxide (N₂O) formed arises mainly from one molecule of NO and one molecule of NH₃. Equivalent results have been reported for experiments carried out in the absence of oxygen;^{4,6-8}

in these investigations minor quantities of N₂ and N₂O were formed, probably by reaction paths 5 and 6. Miyamoto et al.⁴ studied the reaction of ¹⁵NO and NH₃ on unsupported V₂O₄ at 350 °C. They found in the exhaust N¹⁵N and N¹⁵NO as well as large amounts of ¹⁵N₂, the latter coming from the reduction of ¹⁵NO by the V₂O₄ catalyst. From these results, we conclude that the reduced supported V₂O₅ catalysts of this work cannot be compared with unsupported V₂O₄ with respect to the behavior during the reaction of NO and NH₃ in the absence of oxygen. With respect to the reoxidation of the reduced sites of the catalyst, NO competes with O₂. However, the reaction of oxygen is faster than the reaction of nitric oxide with the catalyst.^{1,2} In the absence of oxygen, two "types" of N₂ and N₂O were formed from the reaction of NO or of NO and NH₃ with the catalyst according to the reactions 3-6 as shown in Figure 6. Three "types" of nitrogen were formed: (i) from the reaction of NO and chemisorbed ammonia (reaction 3); (ii) from the oxidation of NH₃ (reaction 1 and 2); and (iii) from the reduction of NO to N₂ (reaction 5). The selectivity of the second reaction, the oxidation of NH₃ to N₂, appears to be determined by the probability that two chemisorbed nitrogen species are adsorbed on adjacent sites. In the presence of oxygen, the third reaction does not occur. Species J shows NO coordinated via its oxygen end to an oxygen vacancy on the catalyst, analogous to the adsorption of nitric oxide on cerium oxide as reported by Niwa et al.¹⁰ They observed that, on a partially reduced site, NO forms a chelating NO₂ species and that the hyponitrite ion as another adsorbed species was a precursor of N₂ and N₂O by adsorption of NO. However, more data and studies are needed in order to establish this surface arrangement.

Oxygen Exchange between NO and the Catalyst. N¹⁸O comes exclusively from scrambling of NO with the surface.² Extra evidence for this conclusion is the lack of ¹⁵N¹⁸O during the experiments. The amount of N¹⁸O at the outlet of the reactor is independent of the specific surface area or the amount of catalyst used. It probably depends on the number of oxygen vacancies adjacent to lattice ¹⁸O. From kinetic measurements with a continuous stirred tank reactor, we have previously found a reaction order of 0.7 for NO, which suggests interaction of NO with the surface. Shelef⁹ observed that the whole monolayer of oxygen and even some subsurface oxygen ions can be exchanged at increasing temperatures. He suggested that surface nitrite ions or nitro complexes served as surface intermediates. The present results show that N¹⁸O can be formed when ¹⁸O₂ is used in the gas phase after ¹⁸O has been built into the surface oxygen layer of the catalyst. The N¹⁸O formed reacts with NH₃ via the Eley-Rideal mechanism as was suggested in our previous paper,² forming N₂ and H₂¹⁸O. From the reaction



it follows that the stoichiometric ratio of H₂O to H₂¹⁸O should be 2. This ratio was found to have values of about 1.2 and 1.6 for the unsupported V₂O₅ and V₂O₅ on TiO₂ catalysts respectively; however, for the other three catalysts, the value was between three and five (Table II). From this, it can be calculated, for the cases of the unsupported V₂O₅ and of V₂O₅ on TiO₂, that the contribution of the reaction of N¹⁸O and NH₃ to give H₂¹⁸O are about 18% and 8%, respectively; it can also be calculated that 90 and 40 ppm, respectively, of NO were converted to N¹⁸O during the reaction. It can thus be concluded that NO interacts with the surface during the selective reduction reaction.

Formation of N₂O. The amount of N₂O produced is inversely proportional to both the oxygen concentration and the specific surface area. If the surface area is smaller, the density of adjacently adsorbed nitric oxide molecules increases to a point where denitration and consequent formation of N₂O sets in (reaction

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5). On the catalyst V_2O_5 on TiO_2 , small amounts of N_2 and N_2O were formed (Table II); this results from the reoxidation of the reduced catalyst surface with NO according to reactions 5 and 6 of Figure 6. Going from V_2O_5 ($S_{BET} = 10.5 \text{ m}^2/\text{g}$) to V_2O_5 on TiO_2 ($S_{BET} = 45 \text{ m}^2/\text{g}$) the selectivities of $N_2^{18}O$ toward N_2O and $^{15}NN^{18}O$ toward ^{15}NNO decrease 50%. This implies that in case of a lower surface area, lattice oxygen becomes more and more involved in the production of N_2O . The density of vacancies is thus enhanced.

Conclusions

A more detailed mechanism based on the experimental results with nitrogen and oxygen tracers has been proposed for the reaction of NO with NH_3 in the presence of oxygen. Almost every phenomenon observed could be explained by the proposed reaction mechanism.

(i) During the reduction reaction most of the N_2 and of the N_2O are formed from the nitrogen atoms of nitric oxide and ammonia for reaction both in the presence of and in the absence of oxygen. The N_2O molecule formed consists primarily of the atoms from one molecule of NO attached to a nitrogen atom from NH_3 .

(ii) It is suggested that two molecules of NO adsorb on a doublet oxygen vacancy with simultaneous release of N_2 and N_2O into the gas phase. When molecular oxygen is present, the formation of N_2 and N_2O from NO is suppressed. Under reducing conditions, some N_2 is formed from NO and under oxidizing conditions, N_2 is formed from ammonia.

(iii) During the reduction reaction, NO shows scrambling with the surface of the catalyst and ammonia is oxidized to molecular nitrogen. This phenomenon is currently being studied further by using labeled NO.

(iv) N_2O is produced from the reaction of one molecule NO with the nitrogen atom from ammonia on two different sites of the catalysts by a reaction sequence involving gaseous nitric oxide and chemisorbed ammonia and by denitration of the surface. The same holds for the formation of water, which is produced by dehydration of the catalyst surface, as a result of the reaction of NO and NH_3 .

(v) The oxygen vacancies are reoxidized more rapidly by O_2 than by NO; this explains the enhancing effect of oxygen on the rate of the overall reaction of NO, NH_3 , and O_2 .

Registry No. NO, 10102-43-9; NH_3 , 7664-41-7; O_2 , 7782-44-7; V_2O_5 , 1314-62-1; TiO_2 , 13463-67-7.

Physical Adsorption on Patchwise Heterogeneous Surfaces. 5. Phase Transitions in Krypton Films on Graphitized Carbon Black in the Temperature Range 104–129 K

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Adsorption isotherms of krypton on graphitized carbon black were measured with a high-precision volumetric adsorption apparatus in the temperature range of 104.5–129.0 K. Three of the isotherms were measured up to more than five statistical adsorbed layers. Isosteric heats and equilibrium spreading pressures were calculated from the adsorption isotherms and aided interpretation of the data. The existence of both a fluid to in-registry solid and an in-registry solid to out-of-registry solid phase transition in the adsorbed krypton films is clear below 122 K. At temperatures of 122 K and above the fluid krypton changes continuously to the out-of-registry solid. Thus, a phase diagram enclosing the in-registry solid adsorbed film was defined. The dispersion force contribution to the surface free energy of graphitized carbon black was calculated to be 154.7 mN/m.

I. Introduction

Experimental studies of gas adsorption have revealed a variety of phase transitions in the adsorbed films¹⁻⁴ if the substrate is nearly "homogeneous".³ One such solid substrate is graphite. Graphitized carbon black (gcb) and some of its variations expose almost exclusively the (0001) lattice plane and consequently have nearly homogeneous surfaces.

If the dimension of the adsorbed gas molecule is compatible with that of the graphite lattice, there may be more than one two-dimensional solid phase. It has been observed that, near the completion of a monolayer, adsorbed krypton may form a two-dimensional solid in-registry with the graphite lattice^{5,6} as well as a close-packed film. The phase transition from two-dimensional (2-D) fluid to 2-D in-registry solid, and the rearrangement of the 2-D in-registry solid to form a close-packed film, appear as two steps on the vapor pressure isotherms near the coverage corresponding to monolayer completion. These transitions were first observed by Thomy and Duval,¹ then by Larher,² and, in this laboratory, by Putnam and Fort³ over a temperature range from 77.3 to 108.7 K.

The present work was intended primarily to extend our study of krypton adsorption on graphitized carbon black to higher temperatures in an attempt to find the temperature above which we postulated⁶ that the adsorbed 2-D fluid crystallizes directly to the adsorbed 2-D close-packed solid. It was also our goal to define more carefully the part of the 2-D phase diagram which enclosed the registered solid phase.⁶ Finally, from determination of spreading pressures for adsorbed krypton films up to pressures near saturation, we wanted to confirm our previously reported³ estimate for the dispersion force contribution to the surface energy of graphitized carbon black.

To these ends, seven new adsorption isotherms were obtained in the temperature range of 104–129 K. Three of the isotherms were measured up to more than five statistical adsorbed layers. Special attention was paid to the phase transition portion of the isotherms, namely, the range of coverage from 100 to about 135

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