The origin of $^{15}NH_3$ produced from the reaction of $^{14}NH_3$ and ^{15}NO over vanadia-based SCR catalysts

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The effects of H_2O and the vanadia content of the catalyst on the formation of $^{15}NH_3$ during the reaction of ^{15}NO and $^{14}NH_3$ in the absence of O_2 over V_2O_5-based catalysts have been determined by mass spectrometry and Fourier transform infrared spectroscopy. At 450°C, the contribution of $^{15}NH_3$ to the total nitrogen-containing products remains constant at about 20% for water concentrations from 0 to 1.6%. The vanadia content also has little effect on the proportion of $^{15}NH_3$ produced. Combination reactions producing $^{14}N^{15}N$ and $^{14}N^{15}NO$ consume surface oxygen species and oxygen mass balances indicate that the amount of $^{15}NH_3$ formed is determined by the extent of these combination reactions. Small concentrations of O_2 (<300 ppm) were sufficient to prevent the formation of $^{15}NH_3$. The reduction of NO by H_2 was also studied. Negligible amounts of NH_3 were formed under dry feed conditions, whereas, in the presence of 1.6% H_2O, $^{15}NH_3$ represents about one third of the products. A mechanism involving reaction of an adsorbed N_s species with H_2O is used to account for these experimental observations.

Keywords: selective catalytic reduction; nitrogen oxides; isotopic labelling; vanadia–titania catalysts

1. Introduction

The mechanism of the selective catalytic reduction reaction (SCR) between NO and NH_3 has been extensively studied [1]. Flue gases typically contain ~ 6% O_2 [1],

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and consequently less attention has been given to reactions that occur in the absence of O_2. These studies without oxygen are of general interest since they indirectly serve to illuminate the role of O_2 in the SCR reaction. Our recent investigation of the reaction between ^{15}NO and $^{14}NH_3$ over V_2O_5/TiO_2 catalysts [2] showed that $^{14}N^{15}N$ and $^{14}N^{15}NO$ were the dominant forms of nitrogen and nitrous oxide produced when O_2 was not present. Very surprisingly, an additional species $^{15}NH_3$ was observed [2], which represented $\sim 20\%$ of the nitrogen-containing products. The $^{15}NH_3$ was not formed by direct exchange between $^{14}NH_3$ and ^{15}NO since no ^{14}NO was produced.

It was suggested that ^{15}NO is broken down into separate ^{15}N and oxygen species on reduced surface sites, and that the ^{15}N species reacts with water to form $^{15}NH_3$ [2]. The aim of this work was to further investigate the mechanism of the direct conversion of NO to NH_3 which occurs over vanadia-based catalysts in the absence of gas phase O_2. Specific aims were to determine the effect of (a) water concentration, and (b) vanadia content on the relative contribution of $^{15}NH_3$ to the products of the $^{15}NO/^{14}NH_3$ reaction.

Formation of ammonia during the reduction of NO with H_2 over metal oxide catalysts has been reported previously [3–6]. The contribution of NH_3 to the total N-containing products varies with the type of catalyst. Kobylinski and Taylor [6] found that for Cr_2O_3/Al_2O_3, the nitrogen-containing products consisted of 97% N_2 and 3% NH_3, whereas supported iron oxide produced 30% N_2 and 70% NH_3. They have also reported the formation of ammonia from NO reduction with CO in the presence of water for these catalysts [6]. It was suggested that the water–gas shift reaction produces H_2, which then reacts with NO to form NH_3.

It is thus possible that a reduced surface and a source of hydrogen, such as H_2, surface hydroxyls or H_2O, are the only requirements for the conversion of NO to NH_3. Hence, experiments were performed under both dry and wet feed conditions to determine whether added water was necessary for the formation of ammonia during the reaction of ^{14}NO and H_2 over V_2O_5/TiO_2. Finally, previous work has shown [7] that $^{15}NH_3$ is not formed during the reaction of ^{15}NO and $^{14}NH_3$ in the presence of excess O_2. In this study, we also determined the effect of small oxygen concentrations (<300 ppm) on the formation of $^{15}NH_3$.

2. Experimental

The preparation of the catalysts and the analysis techniques used in this study have been reported in detail elsewhere [2], and a summary only is included here. Catalysts were prepared by incipient wetness impregnation, and then dried in air at 60°C and calcined at 500°C for 3 h. After calcination the catalysts were crushed and the 300–500 μm fraction separated for use. BET surface areas of the catalysts were determined by N_2 adsorption at −196°C. X-ray diffraction (XRD) patterns were measured with a Philips PW1700 automated powder X-ray diffractometer.

Diffraction patterns were recorded with Cu Kα radiation using a step interval of 0.02° (2θ) with a count time of 0.8 s per step over an angular range 2–70° (2θ). Vanadium contents were determined by inductively coupled plasma–atomic emission spectrometry (ICP-AES) after digestion in sulphuric acid.

Catalytic testing was carried out in a continuous flow system at atmospheric pressure. The feed streams were made from standard gas mixtures in He diluent. When hydrogen was used as the reductant, a small flowrate of a H_2/Ar (10.4% H_2) mixture was introduced in place of the NH_3/He. The concentration of O_2 in the reactants was less than 5 ppm. When desired, water could be introduced into the reactant mixture by diverting the He stream through a standard laboratory glass water bubbler equipped with a sintered frit and immersed in a constant temperature water bath. A range in water vapour pressures was obtained by varying the bath temperature. Background levels of H_2O in the absence of added water were ~ 0.05% and arose, for the most part, from the NH_3/He standard mixture. The reactants were passed over 50–200 mg of catalyst heated to 350–450°C. Details of the catalyst masses and flowrates are given in tables 1 and 2.

The exit gas was monitored continuously by a mass spectrometer with periodic sampling for analysis by gas chromatography and off-line Fourier transform infrared (FTIR) spectroscopy. The steady-state activity and selectivity of the catalysts at each condition were first determined using unlabelled mixtures ($^{14}NO/^{14}NH_3$ before substituting ^{14}NO with ^{15}NO (Isotec Inc., 99.4% ^{15}N) and, after the switch to ^{15}NO was made, the reaction was continued until the mass spectrometer signals were stable. General details of the FTIR and MS procedures are given in refs. [2,7].

FTIR was used to assess the amounts of ^{14}NO and $^{15}NH_3$ formed by the reaction itself, and of $^{14}N^{15}NO$ versus $^{15}N^{14}NO$. Direct $^{15}NO/^{14}NH_3$ isotopic exchange was discounted as $^{15}NH_3$ and ^{14}NO were never observed in the infrared spectra concurrently. Conversions of ^{15}NO were determined from the mass spectral analyses of $m/e = 31$. Conversions of $^{14}NH_3$ are less certain due to a contribution from fragment ions of H_2O ($m/e = 18$) and $^{15}NH_3$ ($m/e = 18$). Therefore, conversions of $^{14}NH_3$ were calculated from the FTIR measurements using the sR ($J = 10$) line at 1176.6 cm^{-1}. Concentrations of $^{15}NH_3$ were determined from the FTIR measurements using the line at 849.1 cm^{-1}.

3. Results

3.1. FORMATION OF $^{15}NH_3$ DURING THE REACTION OF ^{15}NO AND $^{14}NH_3$

The results of table 1 reveal the effect of water on the reaction of ^{15}NO and $^{14}NH_3$ in the absence of oxygen over 1.8 wt% V_2O_5/TiO_2. The isotopic product distribution observed in the absence of added water (i.e. in the presence of about 0.05% H_2O) is consistent with that reported previously [2]. The absolute concentra-

Table 1
The effect of water, vanadia content and small O_2 concentrations on the isotopic product distributions

Catalyst	Temp. (°C)	Concentration		Mass of catalyst (mg)	Flowrate (ml/min)	Conversion (%)			Selectivity to N_2O (%)
		O_2 (ppm)	H_2O (%)			^{15}NO	$^{14}NH_3$ [a]	O_2	
V_2O_5/TiO_2	450	<5	0.05	50	40	64	34	– [e]	13
(1.8 wt% V_2O_5)	450	<5	0.34	50	40	32	15	–	6
	450	<5	1.60	50	40	18	11	–	2
V_2O_5	350	<5	0.05	50	40	30	14	–	40
(100 wt% V_2O_5)	450	<5	0.05	50	80	76	40	–	37
V_2O_5/TiO_2	350	<5	0.05	250	40	73	45	–	23
(1.7 wt% V_2O_5)	350	275	0.05	25 [d]	160	56	52	41	7

[a] $^{14}NH_3$ conversion determined by FTIR spectroscopy.
[b] Calculated from the product distribution by eq. (5).
[c] Calculated from the product distribution ($^{14}N^{15}N + ^{14}N^{15}NO + 2(^{15}N_2 + ^{15}N_2O) + ^{15}NH_3$(FTIR)).
[d] 25 mg V_2O_5/TiO_2 diluted with 25 mg of TiO_2.
[e] – indicates not applicable.

tion of $^{15}NH_3$ decreases significantly with increasing water concentration. Note, however, that a similar decrease in the conversions of ^{15}NO and $^{14}NH_3$ is also observed. The final column of table 1 gives the amount of $^{15}NH_3$ expressed as a percentage of the total ^{15}NO reacted (calculated from the isotopic product distribution). Interestingly, this value remains approximately constant at ~ 20% for water concentrations between 0.05% and 1.6%. Thus, $^{15}NH_3$ formation decreases in proportion to the change in ^{15}NO conversion. This trend is better illustrated by fig. 1 which shows the relative contribution of the major species ($^{14}N^{15}N$, $^{15}NH_3$ and $^{14}N^{15}NO$) to the total nitrogen-containing products as a function of H_2O concen-

Table 2
The effect of water on the product distributions for the reaction of ^{14}NO (800 ppm) and H_2 (5200 ppm) in the absence of oxygen over V_2O_5/TiO_2

Catalyst	Temp. (°C)	Mass of catalyst (mg)	Flowrate (ml/min)	H_2O conc. (%)	Conversion (%)		Selectivity to N_2O (%)	Product distribution (ppm)			NH_3/NO reacted [b] (%)
					NO	H_2		N_2	N_2O	NH_3 [a]	
V_2O_5/	450	200	40	0.05	38	7	21	110	30	5	3
TiO_2 [c]	450	200	40	1.60	23	5	4	62	5	60	31

[a] By FTIR spectroscopy.
[b] Calculated from the product distribution (2(N_2 + N_2O) + NH_3).
[c] 3.4 wt% V_2O_5.

(Table 1 continued)
for the reaction of ^{15}NO and $^{14}NH_3$ over V_2O_5-based catalysts

Product distribution (ppm)						$^{15}NH_3$ (ppm)			$^{14}N^{15}NO$/ ($^{14}N^{15}N$+ $^{14}N^{15}NO$) (%)	$^{15}NH_3$/ ^{15}NO reacted [c] (%)
nitrogens			nitrous oxides			^{15}N mass balance	FTIR	oxygen[b] balance		
$^{14}N_2$	$^{14}N^{15}N$	$^{15}N_2$	$^{14}N_2O$	$^{14}N^{15}NO$	$^{15}N_2O$					
−8	323	12	−2	55	7	86	90	85	12	18
−8	171	−5	−2	13	1	46	48	42	7	21
−9	105	−5	−5	3	0	14	23	23	3	18
8	74	6	2	92	7	86	66	75	59	26
29	207	14	5	183	42	207	145	166	47	22
23	364	7	11	101	8	122	96	170	22	19
−5	399	−19	3	25	0	–	<5	–	6	–

tration. It can be seen that the relative amount of $^{15}NH_3$ is independent of the water concentration and conversion level.

Some other effects of added water are also observed. Selectivity to N_2O decreases from 13 to 2% for an increase in the water concentration from 0.05 to 1.6%. Fig. 1 shows that the decrease in the relative amount of $^{14}N^{15}NO$ produced is accompanied by a corresponding increase in the proportion of $^{14}N^{15}N$. Minor amounts of $^{15}N_2O$ and $^{15}N_2$ are produced under dry feed conditions, however, small amounts (0.34%) of added water are sufficient to prevent the formation of these species. Negligible amounts of ammonia oxidation products, $^{14}N_2$ and $^{14}N_2O$, are produced over 1.8 wt% V_2O_5/TiO_2 with or without added water.

The effect of vanadia content on the formation of $^{15}NH_3$ was investigated by studying the reaction using unsupported V_2O_5. Fig. 2 shows the XRD patterns for unused V_2O_5 and the spent catalyst after reaction in the absence of oxygen at 450°C. The diffraction pattern of the fresh catalyst shown in fig. 2a was confirmed by comparison with the reference pattern for pure V_2O_5 given in fig. 2b. The XRD pattern of the spent catalyst (fig. 2c) was not typical of crystalline V_2O_5, but exhibited features characteristic of V_2O_4 (fig. 2d). Notice that the XRD pattern of the spent catalyst has been magnified by a factor of 3 and does not exhibit any narrow, well-defined peaks, indicating the amorphous nature of the material. Thus, reaction in the absence of oxygen results in the reduction of V_2O_5, probably to V_2O_4. Titania-supported catalysts with vanadia loading less than 6% do not exhibit features due to crystalline V_2O_5 [7,8], and therefore a change in the oxidation state of the monomeric and polymeric species is not easily detected.

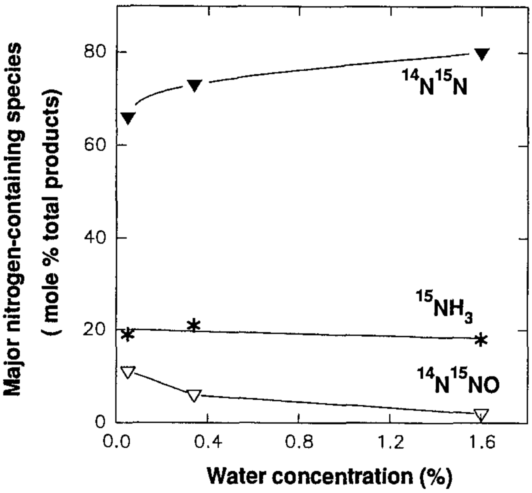

Fig. 1. The effect of water concentration on the distribution of the major N-containing products for the reaction of ^{15}NO and $^{14}NH_3$ in the absence of O_2 at 450°C over V_2O_5/TiO_2 (1.8 wt% V_2O_5. (▼) $^{14}N^{15}N$, (▽) $^{14}N^{15}NO$, (∗) $^{15}NH_3$.

Table 1 also shows the isotopic product distribution observed for unsupported V_2O_5 after reaction under oxygen-free and dry feed conditions. The contribution of $^{15}NH_3$ to the total nitrogen-containing products is similar to that of the supported catalyst. At 450°C and roughly equal conversions, $^{15}NH_3$ represents 22% of the ^{15}NO reacted over V_2O_5 compared to a value of 18% for the V_2O_5/TiO_2 catalyst

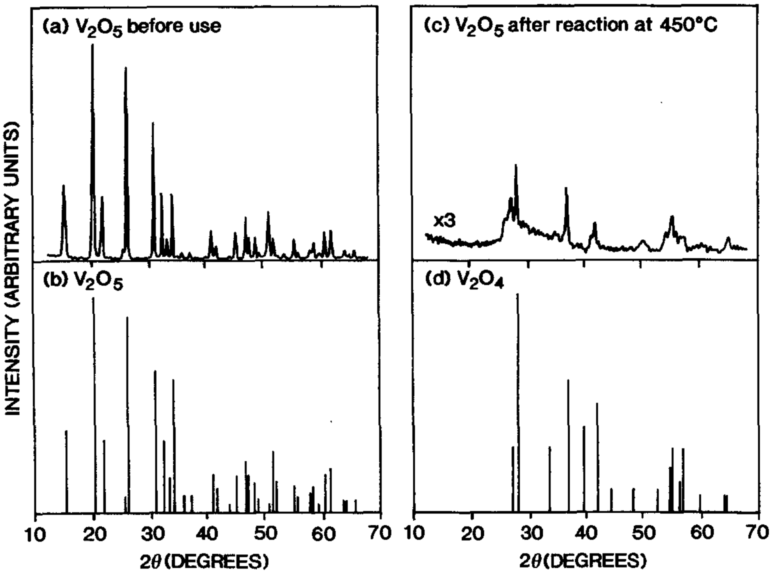

Fig. 2. X-ray diffraction patterns for (a) unused V_2O_5, (b) reference V_2O_5, (c) spent V_2O_5 after reaction of ^{15}NO and $^{14}NH_3$ in the absence of O_2 at 450°C, and (d) reference V_2O_4.

(table 1). There is, however, one important difference. Unlike the situation with the V_2O_5/TiO_2 catalyst, the formation of $^{15}N_2O$ becomes significant over the unsupported catalyst at 450°C. At this temperature, $^{15}N_2O$ represents ~7% of the total products. The formation of products arising from NO decomposition reactions, i.e. $^{15}N_2O$ and $^{15}N_2$, over V_2O_4 has been reported previously [9]. The formation of $^{14}N_2$, which must arise from ammonia oxidation, is also observed over the unsupported material at higher temperatures. ^{14}NO, which is a prominent product at high temperatures when O_2 is present [7], was not detected in the present experiments.

The effect of O_2 concentration on the formation of $^{15}NH_3$ over V_2O_5/TiO_2 is given in the bottom two rows of table 1. The NO and NH_3 reaction is accelerated in the presence of gas phase oxygen, and it was necessary to dilute the V_2O_5/TiO_2 catalyst with TiO_2 to obtain comparable conversion levels. The oxygen concentration was chosen such that the conversion was approximately 50%. There are two features worth noting. Firstly, small gas phase O_2 concentrations (~ 275 ppm) were sufficient to completely suppress the formation of $^{15}NH_3$. Secondly, the ratio of the ^{15}NO and $^{14}NH_3$ conversions is about 1 : 1 when O_2 is added, indicating that (for equimolar inlet concentrations) the products are formed predominantly by the combination reactions, i.e. $^{14}N^{15}N$ and $^{14}N^{15}NO$.

One expects the difference between the amount of ^{15}NO converted and the amount of ^{15}N in the nitrogens and nitrous oxides to equal the amount of $^{15}NH_3$ observed by FTIR. Table 1 compares the amount of $^{15}NH_3$ calculated from ^{15}N mass balances with the values determined directly by FTIR measurements. The agreement is good considering the various errors in the various experimental measurements. Note, that we regard the direct determination of $^{15}NH_3$ by FTIR as considerably more reliable than from the ^{15}N mass balances.

The near constant amount of $^{15}NH_3$ formed, regardless of catalyst and water content, can also be explained in oxygen mass balance terms as follows. Assuming that the oxygen which originates from the reacted nitric oxide leaves the system as product H_2O (not as O_2), the following equations can be written for the formation of $^{14}N^{15}N$ and $^{14}N^{15}NO$:

$$5\,^{14}NH_3 + 6\,^{15}NO \rightarrow 5\,^{14}N^{15}N + {}^{15}NH_3 + 6H_2O \tag{1}$$

$$5\,^{14}NH_3 + 8\,^{15}NO \rightarrow 5\,^{14}N^{15}NO + 3\,^{15}NH_3 + 3H_2O\,. \tag{2}$$

These reactions necessarily imply the concomitant conversion of ^{15}NO to $^{15}NH_3$. If these are the only nitrogen and nitrous oxide species produced, then from the oxygen balance equations (1) and (2), one expects that

$$^{15}NH_3 = \tfrac{1}{5}\,^{14}N^{15}N + \tfrac{3}{5}\,^{14}N^{15}NO\,. \tag{3}$$

Similar equations to (1) and (2) can be written for all the other nitrogen-containing products. The formation of ammonia oxidation products $^{14}N_2$ and $^{14}N_2O$ consumes surface oxygen, whereas the formation of NO decomposition products $^{15}N_2$

and $^{15}N_2O$ supplies oxygen to the catalyst surface. The overall amount of $^{15}NH_3$ expected can be calculated using the following equation:

$$^{15}NH_3 = \tfrac{1}{5}{}^{14}N^{15}N + \tfrac{3}{5}{}^{14}N^{15}NO + \tfrac{6}{5}{}^{14}N_2 + \tfrac{8}{5}{}^{14}N_2O - \tfrac{4}{5}{}^{15}N_2 - \tfrac{2}{5}{}^{15}N_2O\,. \tag{4}$$

Table 1 compares the values for $^{15}NH_3$ produced (determined from FTIR spectroscopy) with those calculated by ^{15}N and oxygen (eq. (4)) mass balances. Good agreement is observed, and this suggests that the conversion of ^{15}NO to $^{15}NH_3$ is determined by the extent of these combination reactions (i.e. surface oxygen requirements, and not by the amount of water or the vanadia content.

3.2. THE NO AND H_2 REACTION

Fig. 3 shows the NO conversion, and product concentrations, for the reaction of NO (~ 900 ppm) and H_2 (~ 5200 ppm) under dry feed conditions over 3.4 wt% V_2O_5/TiO_2. Product distributions and experimental details are given in table 2. In the absence of added water, negligible amounts (< 5 ppm) of NH_3 were produced at all temperatures below 450°C. Additionally, the results of table 2 show that, for

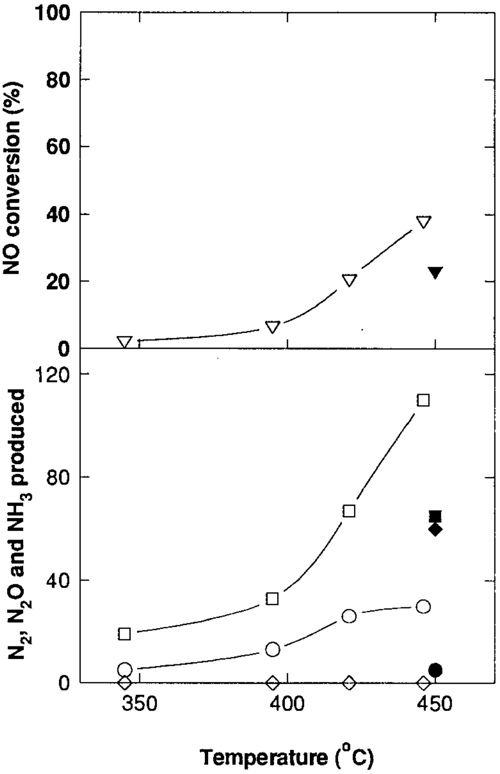

Fig. 3. NO conversion and N-containing products as a function of temperature for the reaction of NO and H_2 in the absence of O_2: (□) N_2, (○) N_2O, (◇) NH_3. Filled symbols are for the reaction in the presence of 1.6% H_2O.

reaction of NO and H_2 at 450°C, four times the catalyst mass was needed to reach a conversion about one-half that observed for the NO and NH_3 reaction (see table 1). This indicates that the reduction of NO by H_2 is about an order of magnitude slower than the reaction between NO and NH_3.

Both fig. 3 and table 2 show that water has a dramatic effect on the products of the NO/H_2 reaction at 450°C. There are two important features. Firstly, water addition causes a marked increase in the amount of NH_3 produced. Under dry feed gas conditions, NH_3 represents less than 3% of the nitrogen-containing products, whereas in the presence of 1.6% H_2O, NH_3 represents about one third of the products. Secondly, water suppresses the formation of nitrous oxide much more than that of nitrogen.

4. Discussion

There have been a number of suggestions of detailed mechanisms for the reaction between NO and NH_3 over V_2O_5/TiO_2 catalysts [1]. It is inappropriate here to discuss these in detail; however, in a previous study, we presented a general framework which draws on these previous suggestions [1] and accounts for our results [7] in excess oxygen. In the presence of oxygen, it is generally accepted [1,8] that nitrogen is formed according to the following two steps:

$$^{14}NH_3 + V{=}O \rightarrow V{-}OH + {}^{14}NH_2(a) \tag{5}$$

$$^{14}NH_2(a) + {}^{15}NO(a) \rightarrow {}^{14}N^{15}N + H_2O\,. \tag{6}$$

The elimination of water follows:

$$2V{-}OH \rightleftharpoons V{=}O + V\square + H_2O \tag{7}$$

(where V□ is a reduced surface site), and if oxygen is present, then reoxidation proceeds readily:

$$2V\square + O_2 \rightarrow 2V{=}O\,. \tag{8}$$

In the absence of O_2, reoxidation must be accomplished by nitric oxide, and the present isotope results indicate that nitrogen atoms so released end up as ammonia ($^{15}NH_3$ when ^{15}NO is used). It is clear that reoxidation by nitric oxide is much slower than that by oxygen since a much larger mass of catalyst is required to achieve the same conversion and 275 ppm of oxygen is sufficient to eliminate $^{15}NH_3$ formation (last two lines of table 1). We have previously suggested [2] that reoxidation by ^{15}NO could be represented by

$$2V\square + V{-}OH + {}^{15}NO \rightarrow 2V{=}O + V{=}{}^{15}NH\,. \tag{9}$$

Hydrolysis of the ^{15}NH group by product water would then give $^{15}NH_3$:

$$V{=}^{15}NH + H_2O \rightarrow V{=}O + {}^{15}NH_3\,. \tag{10}$$

Another possibility is that ^{15}NO may dissociate on a reduced vanadia site to form an adsorbed nitrogen species, $^{15}N(a)$. Indeed, Went et al. [8] have previously suggested that reoxidation by nitric occurs via a process similar to

$$^{15}NO(a) + V_mO_{(2.5m-1)} \rightleftharpoons V_mO_{2.5m} + {}^{15}N(a)\,. \tag{11}$$

Therefore, it is not unreasonable to expect that a $^{15}N(a)$ species, whether nitride-like or covalently bound (V≡N), might also undergo hydrolysis (or reaction with V–OH groups) to form $^{15}NH_3$:

$$2V{\equiv}^{15}N + 3V\square + 3H_2O \rightarrow 3V{=}O + 2^{15}NH_3 \tag{12}$$

$$^{15}N(a) + 3V{-}OH \rightarrow 3V{=}O + {}^{15}NH_3\,. \tag{13}$$

Addition of water reduces the absolute amounts of $^{15}NH_3$ produced, but does not significantly change the ratio of $^{15}NH_3$ produced to that of ^{15}NO reacted (see table 1). This suggests that the effect of added water is to simply reduce the overall rate of the process. In the context of the reaction scheme this can be reconciled with the effect of added water on step (7), in which the reverse reaction is promoted and the surface density of reduced vanadia surface sites (V□) decreases.

Our results for NO reduction by H_2 are readily accommodated within this framework. In the absence of water this reaction produced mainly N_2 and some N_2O. Reduction by hydrogen,

$$2V{=}O + H_2 \rightarrow 2V{-}OH\,, \tag{14}$$

is followed by dehydration of V–OH groups according to step (7), and reoxidation by nitric oxide according to either (9) or (11). The reaction between NO and H_2 is much slower than that between NO and NH_3. Previous workers [10] have also observed that NO reduction with H_2 is slower than with NH_3. It is possible that the reaction between NO and H_2 is at least partly restricted by the reduction step (14) which will reduce the availability of V–OH groups or adsorbed water required for hydrolysis. In this situation, it is more favourable for the nitrogen species to leave the surface as nitrogen or nitrous oxide according to

$$N(a) + N(a) \rightarrow N_2 \tag{15}$$

$$N(a) + NO(a) \rightarrow N_2O\,. \tag{16}$$

There is also good evidence that NO can interact with reduced surfaces of vanadia-based catalysts to give mononitrosyl and dinitrosyl complexes [11–13], thus another possible source of nitrous oxide is

$$NO(a) + NO(a) \rightarrow N_2O + O(a)\,. \tag{17}$$

When water is added, hydrolysis is again competitive and some ammonia is produced (table 2), presumably by processes similar to those given in eqs. (12) and (13).

Nitrous oxide formation in particular is suppressed since water will tend to displace the adsorbed nitric oxide required for eqs. (16) and (17).

A distinctive feature of the ^{15}NO and $^{14}NH_3$ reaction over pure V_2O_5 catalyst, but not the titania-supported material, is the formation of some $^{15}N_2O$ and $^{15}N_2$ at higher temperatures. This is readily explained in terms of eqs. (15)–(17) and the above arguments. It is less likely to occur with supported catalysts since the sites are more widely spaced. The more important nitrous oxide species produced with both pure and supported V_2O_5 is $^{14}N^{15}NO$, which must arise by another route. Went et al. [8] suggest

$$NH_2(a) + NO(a) + V_mO_{2.5m} \rightarrow N_2O(g) + H_2O(g) + V_mO_{(2.5m-1)}\,, \qquad (18)$$

which involves the same ammonia fragment from which nitrogen is formed (eq. (6)). An alternative view which we have previously suggested [7] is that, at higher temperatures, an additional hydrogen may be abstracted to form ^{14}NH and that it is this species which yields the nitrous oxide by reaction with $^{15}NO(a)$:

$$^{14}NH(a) + {}^{15}NO(a) + V{=}O \rightarrow {}^{14}N^{15}NO + V{-}OH\,. \qquad (19)$$

It is, of course, possible to suggest alternative mechanisms for product formation in these systems. However, we believe that our suggested scheme provides a consistent framework for the observed products of reactions between NO and NH_3 in the presence and absence of O_2 and for those between NO and H_2. It also accounts for the effects of water on the product distributions, and for the ability of small concentrations of O_2 to prevent $^{15}NH_3$ formation.

5. Conclusions

(1) The contribution of $^{15}NH_3$ to the total nitrogen-containing products of the reaction of ^{15}NO and $^{14}NH_3$ in the absence of O_2 is independent of the water concentration. For H_2O concentrations between 0.05 and 1.6%, $^{15}NH_3$ represents about 20% of the ^{15}NO reacted.

(2) For pure V_2O_5 at 350°C, the product distribution is similar to that for the titania-supported catalyst, $^{15}NH_3$ again representing about 20% of the total nitrogen-containing products. However, a distinctive feature of the reaction over pure V_2O_5 is that decomposition of nitric oxide to $^{15}N_2O$ becomes significant at 450°C.

(3) Oxygen mass balances indicate that the O_2 required for the formation of $^{14}N^{15}N$ and $^{14}N^{15}NO$ is supplied by the direct conversion of ^{15}NO to $^{15}NH_3$. Small amounts of gas phase oxygen (<275 ppm) are sufficient to prevent the formation of $^{15}NH_3$.

(4) For the reaction of ^{14}NO and H_2, no $^{15}NH_3$ is produced under dry feed conditions. However, in the presence of 1.6% water, $^{15}NH_3$ represents about one third of the nitrogen-containing products. This suggests that H_2O, or some form of hydroxylated surface, is necessary for the formation of $^{15}NH_3$.

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