

^{15}N -Labelling Studies of the Effect of Water on the Reduction of NO with NH_3 over Chromia SCR Catalysts in the Absence and Presence of O_2

Bronwyn L. Duffy,* H. Edward Curry-Hyde,*¹ Noel W. Cant,[†] and Peter F. Nelson \ddagger ¹

*School of Chemical Engineering and Industrial Chemistry, P.O. Box 1, Kensington, New South Wales 2033, Australia; [†]School of Chemistry, Macquarie University, New South Wales 2109, Australia; and \ddagger CSIRO Division of Coal and Energy Technology, P.O. Box 136, North Ryde, New South Wales 2113, Australia

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Activity studies and isotopic labelling experiments have been performed to determine the effect of water on the reaction of NO and NH_3 , in the absence and presence of oxygen, for both amorphous and crystalline ($\alpha\text{-Cr}_2\text{O}_3$) chromia catalysts. The products of the reaction of ^{15}NO and $^{14}\text{NH}_3$ were determined using mass spectrometry, Fourier transform infrared spectroscopy, and gas chromatography. In the presence of excess (1.8%) O_2 , the addition of 1.5% H_2O decreases NO and NH_3 conversions over amorphous chromia for all temperatures below 275°C. For $\alpha\text{-Cr}_2\text{O}_3$, the effect of water varies with reaction temperature: at temperatures less than 225°C, NO conversion is lower with water present, whereas above 225°C, higher NO conversions are observed under wet gas conditions. The effect of water on activity and selectivity is reversible. Labelling experiments show that water addition significantly decreases the formation of products arising from ammonia oxidation reactions. The formation of $^{14}\text{N}_2\text{O}$ and ^{14}NO is completely inhibited for both forms of chromia. For $\alpha\text{-Cr}_2\text{O}_3$, $^{14}\text{N}_2$ is the dominant form of nitrogen under dry feed conditions. Increasing water vapour pressures suppress the formation of $^{14}\text{N}_2$, and $^{14}\text{N}^{15}\text{N}$ becomes the dominant nitrogen species in the presence of 1.5% H_2O . Increasing amounts of water favour the formation of $^{14}\text{N}^{15}\text{N}$ relative to that of $^{14}\text{N}^{15}\text{NO}$ for both amorphous chromia and $\alpha\text{-Cr}_2\text{O}_3$. In the absence of O_2 , the activity and selectivity of both amorphous and $\alpha\text{-Cr}_2\text{O}_3$ is markedly affected by the presence of small concentrations (0.5%) of added H_2O , the effect being much more significant than in excess O_2 . Unlike reaction in the presence of oxygen, the selectivity to nitrous oxide increases with added water; however, the relative proportions of $^{14}\text{N}^{15}\text{NO}$ and $^{15}\text{N}_2\text{O}$ (the main nitrous oxide species) remain constant. A tentative mechanism, which can account for the observations, is given. © 1995 Academic Press, Inc.

INTRODUCTION

Selective catalytic reduction (SCR) with ammonia is the most effective, and the only commercially practised, catalytic technology for the post-combustion control of

emissions of nitrogen oxides (NO_x) from stationary sources (1). Development of an active low-temperature SCR catalyst is attractive because it may allow greater flexibility in the placement of the SCR reactor in the flue gas stream and thus has the potential to reduce overall cost and improve efficiency. Amorphous chromia (2) has been shown to be a highly active and selective catalyst for the reduction of nitric oxide with ammonia in the presence of excess O_2 for temperatures below 180°C. The performance of chromia catalysts is, however, dependent on the crystalline form since, by contrast, crystalline chromia ($\alpha\text{-Cr}_2\text{O}_3$) gives rise to substantial nitrous oxide at all temperatures and also exhibits considerable activity for ammonia oxidation (2–5), both of which are undesirable effects.

Most flue gases containing NO_x also contain large volumes of water (2–18%). While the majority of laboratory studies of SCR catalysts have been conducted under dry conditions, a limited amount of work on the effect of water has been reported. However, some of these reports present conflicting results concerning the effect of H_2O for various catalysts (6–13). Early durability tests by Bauerle *et al.* (6, 7) found that water concentrations between 0–20% did not affect NO conversion for $\text{Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ (6) and $\text{V}_2\text{O}_5/\text{TiO}_2$ (7) catalysts. However, later studies by Willey *et al.* (8) and Tufano and Turco (9) on the kinetics of the NO and NH_3 reaction for iron oxide–chromia and vanadia–titania catalysts, respectively, showed a decrease in the rate of NO reduction in the presence of H_2O . A number of studies (10, 11) reported that water reduced the conversion of NO over supported vanadia catalysts. More recently, two studies report the effect of water on the reaction of NO and NH_3 over vanadia-based catalysts (12, 13) as a function of temperature. Water was found to decrease the NO conversion at temperatures below 330°C for a 30 wt% $\text{V}_2\text{O}_5/\text{SiO}_2/\text{TiO}_2$ catalyst (12) and below 390°C for a 6 wt% $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst (13). The decrease in NO reduction activity in

¹ To whom correspondence should be addressed.

the presence of water is a possible limitation to low temperature operation of SCR catalysts.

Several workers have attributed the inhibiting effect of water to the competitive adsorption of water and ammonia for active sites (8, 9, 12). However, Topsøe *et al.* (13) claim that water does not inhibit the adsorption of ammonia on the vanadia surface under SCR conditions and Ramis *et al.* (14) found that NH_3 was able to displace H_2O from Lewis acid sites on a vanadia-titania surface at room temperature.

The involvement of water in the reaction mechanism under wet conditions is also of interest. Janssen *et al.* (15) suggested that dehydration of the catalyst surface (water is a product in the reaction) is the rate-determining step. Additionally, there is considerable debate as to whether V-OH (16), V=O (17, 18), or some combination of both groups (19, 20) are the active sites for the NO and NH_3 reaction. Miyata *et al.* (21) have suggested that, for $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts, Lewis acid sites are converted to Brønsted acid sites on the introduction of water vapour. Further, Chen and Yang (22) found that dehydroxylation of a $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst by heat treatment destroyed its catalytic activity, which was rapidly restored on exposure to H_2O .

The aim of this work was to investigate the effect of water on the activity and selectivity of the reaction of NO and NH_3 over unsupported amorphous chromia and $\alpha\text{-Cr}_2\text{O}_3$ in both the presence and absence of O_2 . By using ^{15}N -isotopic labelling techniques it is possible to determine whether H_2O addition has a greater effect on the combination reactions of ^{15}NO and $^{14}\text{NH}_3$ or the ammonia oxidation reactions. Only the labelling experiments of Janssen *et al.* (23) and Vogt *et al.* (24, 25) for vanadia-containing catalysts and Duffy *et al.* (26) for chromia catalysts have used experimental conditions typical of industrial applications. None, however, has been conducted under wet gas conditions. The present work has employed a continuous flow system with low reactant pressures (<1000 ppm), water concentrations up to 1.8%, and oxygen concentrations of 0 and 1.8%.

EXPERIMENTAL METHODS

Catalytic testing was carried out in a continuous flow system in a manner described in detail elsewhere (26). In essence NO and NH_3 (each with a nominal concentration of 900 ppm) and O_2 (1.8%), diluted with helium, were passed over 50 to 200 mg of catalyst contained in a 5-mm i.d. quartz tube heated to temperatures between 140 and 300°C. Water was introduced to the reactant mixture by passing the combined O_2 and He streams through a standard laboratory glass bubbler equipped with a sintered frit and immersed in a constant temperature water bath. The bath temperature was varied in order to obtain a

range of vapour pressures. Background levels of water in the dry feed gas were $\approx 0.05\%$ and arose, for the most part, from the NH_3/He standard mixture. The exit gas was monitored continuously by a mass spectrometer with periodic sampling for analysis by gas chromatography and Fourier transform infrared (FTIR) spectroscopy. In experiments with ^{15}NO (Isotec Inc., 99.4% ^{15}N) the catalyst was first run to a steady state with a $^{14}\text{NH}_3/^{14}\text{NO}$ mixture and, after the switch to ^{15}NO was made, the reaction was continued until the mass spectrometer signals were stable. Conversions of ^{15}NO were determined from the mass spectral analyses at $m/e = 31$ and $^{14}\text{NH}_3$ conversions were obtained from FTIR measurements using the sR ($J = 10$) line of $^{14}\text{NH}_3$ at 1176.6 cm^{-1} . In most cases, mass spectral and gas chromatographic analyses for total nitrogens and for total nitrous oxides agreed to within $\pm 5\%$. Before any activity measurements were performed, the catalyst was preconditioned with the appropriate reaction mixture for a minimum of 12 h. During isotopic labelling investigations, the steady state activity and selectivity of the catalyst under each condition were first determined using unlabelled reactants (^{14}NO and $^{14}\text{NH}_3$) before substituting ^{15}NO for ^{14}NO to obtain the isotopic product distribution.

The chromia catalysts were prepared by the addition of aqueous ammonia to a dilute solution of chromium (III) nitrate (99% minimum). The resultant precipitates were dried overnight at 100°C in air and later heated in a hydrogen atmosphere. Amorphous chromia was prepared by heating to a maximum temperature of 380°C (4°C/min, then isothermal for 3 h), whereas $\alpha\text{-Cr}_2\text{O}_3$ was formed by heating to 470°C. The preparations were crushed and sieved to 300–500 μm for the catalytic experiments. The surface areas (N_2 BET) were 55 m^2/g ($\alpha\text{-Cr}_2\text{O}_3$) and 280 m^2/g (amorphous chromia). The amorphous form was microporous with a large fraction of the total area in pores of diameter less than 2 nm. The average pore diameter of the $\alpha\text{-Cr}_2\text{O}_3$ was 30 nm. The crystal structures of the catalysts were confirmed by X-ray diffraction (XRD).

RESULTS AND DISCUSSION

One difficulty encountered with isotopic labelling experiments is that, for species containing two nitrogen atoms, there are three or four possible isotopic species (e.g., N_2O – $^{14}\text{N}_2\text{O}$, $^{14}\text{N}^{15}\text{NO}$, $^{15}\text{N}^{14}\text{NO}$, $^{15}\text{N}_2\text{O}$) which need to be measured. For low conversions it becomes very difficult to measure these species accurately. Thus, in the majority of these experiments, conversions above 30% have been studied. However, one of our earlier papers (26) shows that the isotopic product distribution is largely independent of the level of conversion and more strongly influenced by reaction temperature. Previous workers (3) have reported reaction rates for N_2 and N_2O production

over crystalline and amorphous chromia on both a surface area and a mass basis. The latter data should be consulted to examine the magnitude of the specific rate of NO reaction for these catalysts. Note also that differences in the mass transfer behavior of the two forms of chromia catalysts have been observed. Indeed, we have presented evidence elsewhere (27) that the amorphous chromia is operating under mass transfer limitations at 190°C in the presence of 1.8% oxygen. However, under these conditions changing the particle size from 300–500 μm to 106–150 μm did not result in a significant change in the selectivity to N_2O , in spite of the substantial increase in the NO and NH_3 conversions.

Effect of Water in the Presence of O_2

Figures 1a and 1b show the effect of H_2O vapour addition on the NO and NH_3 conversions, and the selectivities to N_2O , as a function of reaction temperature for amorphous chromia and $\alpha\text{-Cr}_2\text{O}_3$, respectively. For amorphous chromia, addition of 1.5% H_2O significantly decreases both the NO and NH_3 conversion for temperatures below 275°C. However, at 300°C the effect becomes negligible. This may be either a genuine reduction in inhibition with temperature, or may arise as the conversions are then near complete. A significant decrease in the selectivity to N_2O is also observed over the full temperature range.

For $\alpha\text{-Cr}_2\text{O}_3$, the situation is quite different. The presence of water decreases the NH_3 conversion substantially for all temperatures below 300°C. For NO conversions, however, the effect of water changes with reaction temperature. At temperatures less than 225°C, NO conversion is lower with water present, whereas above 225°C higher NO conversions are observed under wet gas conditions.

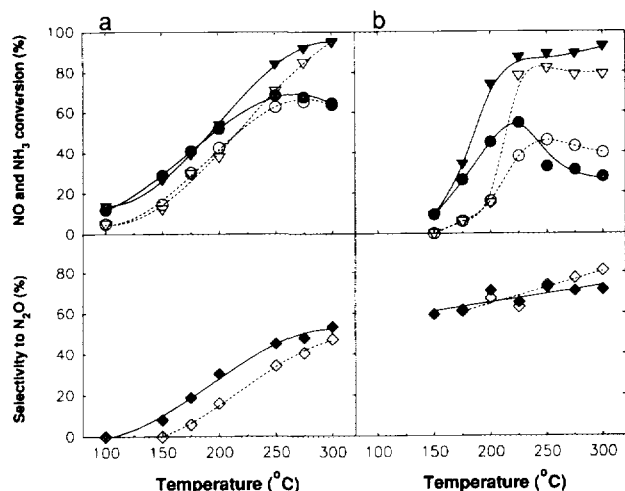


FIG. 1. The effect of water on the conversion of NO and NH_3 , and the selectivity to N_2O , as a function of temperature for (a) amorphous chromia and (b) crystalline $\alpha\text{-Cr}_2\text{O}_3$. (●) NO conversion; (▼) NH_3 conversion; (◆) selectivity to N_2O ; (open symbols) 1.5% H_2O .

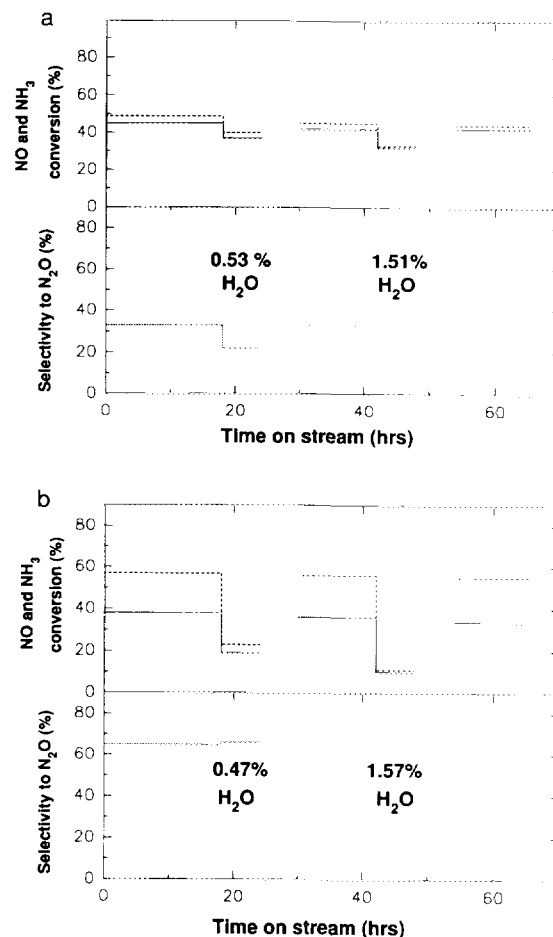


FIG. 2. NO and NH_3 conversions and selectivity to N_2O , as a function of time on stream after being alternately exposed to wet (0.5 and 1.5% H_2O) and dry feed conditions for (a) amorphous chromia and (b) crystalline $\alpha\text{-Cr}_2\text{O}_3$, in the presence of 1.8% O_2 at 190°C. (solid line) NO conversion; (dashed line) NH_3 conversion; (dotted line) selectivity to N_2O .

Thus for $\alpha\text{-Cr}_2\text{O}_3$, it appears that water hinders the ammonia oxidation reactions, but promotes the combination reaction of NO with NH_3 . Unlike the results for amorphous chromia, the overall selectivity to nitrous oxide remains approximately constant.

Experiments were conducted to determine whether water has a permanent effect on catalytic activity. The reaction in the presence of oxygen at 190°C was observed over 70 h, during which time the catalyst was alternately exposed to wet and dry feed conditions. Figure 2 shows the NO and NH_3 conversions and selectivity to N_2O , as a function of time on stream after the addition of $\approx 0.5\%$ and later $\approx 1.5\%$ H_2O . In both cases, the original activity and selectivity are restored when the catalyst is reexposed to the dry feed gas.

The results of Table 1 reveal the effect of H_2O on the reaction of ^{15}NO and $^{14}\text{NH}_3$ over amorphous chromia and

TABLE 1

The Effect of Water on the Reaction of ^{15}NO and $^{14}\text{NH}_3$ in the Presence of Excess (1.8%) Oxygen over Amorphous and $\alpha\text{-Cr}_2\text{O}_3$

Catalyst	Temperature (°C)	Mass of catalyst (mg)	Flow rate (ml/min)	H_2O^a concentration (%)	Conversion		NH_3/NO consumption ratio ^c	Selectivity to N_2O (%)	Product distribution ^a (ppm)						$\frac{^{14}\text{N}^{15}\text{NO}}{^{14}\text{N}^{15}\text{N} + ^{14}\text{N}^{15}\text{NO}}$ (%)	
					$^{15}\text{NO}^a$ (%)	$^{14}\text{NH}_3^b$ (%)			$^{14}\text{N}_2$	$^{14}\text{N}^{15}\text{N}$	$^{15}\text{N}_2$	$^{14}\text{N}_2\text{O}$	$^{14}\text{N}^{15}\text{NO}$	$^{15}\text{N}_2\text{O}$		$^{14}\text{NO}^b$
Amorphous chromia	190	50	40	0.05	68	75	1.19	23	28	429	—	21	118	0	7	21
	190	100	80	1.80	60	58	1.18	11	37	359	—	0	47	0	<5	12
$\alpha\text{-Cr}_2\text{O}_3$	185	100	40	0.05	67	96	1.88	67	173	85	—	55	465	3	30	85
	190	200	80	0.42	48	58	1.49	62	84	77	—	2	264	0	<5	77
	190	200	80	1.50	31	36	1.34	62	39	63	—	1	166	1	<5	72

^a By mass spectrometry.^b By Fourier transform infrared spectroscopy.^c Calculated from the product distribution.

TABLE 2

The Effect of Water on the Reaction of ^{15}NO and $^{14}\text{NH}_3$ in the Absence of Oxygen for Amorphous and $\alpha\text{-Cr}_2\text{O}_3$

Catalyst	Temperature (°C)	Mass of catalyst (mg)	Flow rate (ml/min)	H_2O^a concentration (%)	Conversion		Selectivity to N_2O (%)	Product distribution ^a (ppm)						$\frac{^{14}\text{N}^{15}\text{NO}}{^{14}\text{N}^{15}\text{N} + ^{14}\text{N}^{15}\text{NO}}$ (%)	
					$^{15}\text{NO}^a$ (%)	$^{14}\text{NH}_3^b$ (%)		$^{14}\text{N}_2$	$^{14}\text{N}^{15}\text{N}$	$^{15}\text{N}_2$	$^{14}\text{N}_2\text{O}$	$^{14}\text{N}^{15}\text{NO}$	$^{15}\text{N}_2\text{O}$		$^{14}\text{NO}^b$
Amorphous chromia	280	100	60	0.05	72	34	53	24	160	31	3	103	139	<5	39
	280	150	80	0.54	47	18	72	-8	67	2	-1	77	98	<5	53
$\alpha\text{-Cr}_2\text{O}_3$	280	100	33	0.05	83	44	34	60	267	21	0	40	135	<5	13
	280	200	80	0.36	22	11	55	-11	52	-3	-4	15	49	<5	22

^a By mass spectrometry.^b By FTIR.^c Calculated from the product distribution.

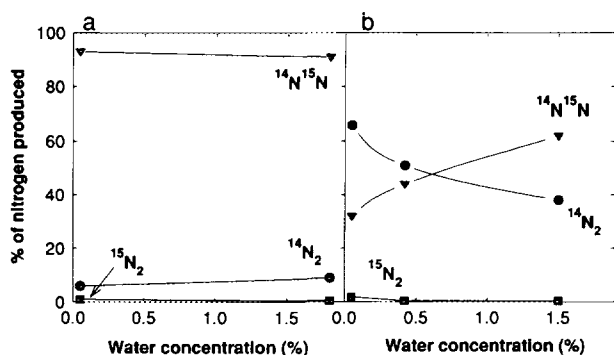


FIG. 3. Internal distribution of the nitrogen species as a function of water concentration at 190°C for (a) amorphous and (b) crystalline α -Cr₂O₃ in the presence of 1.8% O₂. (●) ¹⁴N₂; (▼) ¹⁴N¹⁵N; (■) ¹⁵N₂.

α -Cr₂O₃ in the presence of \approx 1.8% O₂. There is one obvious feature. Small amounts of water completely inhibit the formation of the ammonia oxidation products ¹⁴N₂O and ¹⁴NO (but not completely for ¹⁴N₃) over both amorphous chromia and α -Cr₂O₃. Note that NO decomposition to ¹⁵N₂O and ¹⁵N₂ is negligible over both forms of chromia with or without water present. Previous studies of the chromia catalysts have shown that it is the presence of O₂ which prevents NO decomposition reactions (26).

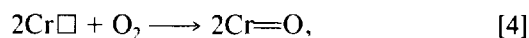
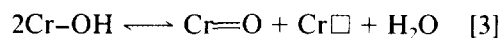
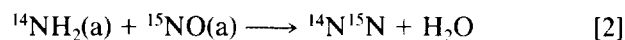
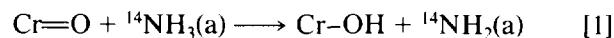
Figure 3 shows the internal isotopic product distributions for nitrogen as a function of water concentration as calculated from the data of Table 1. For amorphous chromia at \approx 200°C, the combination reaction of ¹⁵NO and ¹⁴NH₃ to form ¹⁴N¹⁵N is the major source of nitrogen regardless of H₂O concentration. For α -Cr₂O₃, the results are quite different. Under dry feed conditions, ¹⁴N₂ is the dominant form of nitrogen produced. However, the addition of water inhibits the oxidation of ammonia to ¹⁴N₂, and ¹⁴N¹⁵N becomes the dominant nitrogen species at 1.5% H₂O. Table 1 also shows values for the ratio of NH₃ to NO consumed during the reaction as calculated from the product distribution. For α -Cr₂O₃, this value decreases from 1.88 to 1.34 when 1.5% H₂O is added, consistent with the significant effect of water on the NH₃ oxidation reactions.

The internal product distribution for the nitrous oxide species as a function of water concentration is shown in Fig. 4. The dominant form of nitrous oxide is ¹⁴N¹⁵NO for both catalyst forms at all water concentrations. The final column of Table 1 gives the amount of ¹⁴N¹⁵NO as a percentage of the mixed species (i.e., ¹⁴N¹⁵N + ¹⁴N¹⁵NO). This value clearly decreases with increasing water concentration for both forms of unsupported chromia catalysts. For amorphous chromia, the products are formed largely from the combination reactions of NO and NH₃, and thus, the overall selectivity to N₂O decreases with increases in water concentration (Fig. 2a). However, for α -Cr₂O₃, the increase in the relative amount of nitrogen

formed via the combination reaction of ¹⁵NO and ¹⁴NH₃, i.e., ¹⁴N¹⁵N, is offset by a decrease in the nitrogen formed from ammonia oxidation, i.e., ¹⁴N₂, and thus the overall selectivity to N₂O remains approximately constant (see Fig. 2b).

Our earlier study of chromia catalysts (26) showed that at low temperatures and with 1.8% O₂, nitrogen is formed largely by the selective reaction of NO with NH₃ over both amorphous and α -Cr₂O₃. However, crystalline chromia has a much higher activity for ammonia oxidation. Thus, at \approx 200°C, the major form of nitrogen produced by amorphous chromia is ¹⁴N¹⁵N; whereas for crystalline α -Cr₂O₃, nitrogen is mainly ¹⁴N₂ and is therefore produced largely from ammonia oxidation. The dominant form of nitrous oxide produced in the presence of O₂ over both morphologies of chromia is always ¹⁴N¹⁵NO.

A tentative mechanism (26) was proposed to account for these results and the salient features of this model are presented below. The major steps suggested for the production of nitrogen (¹⁴N¹⁵N) were



where Cr□ represents a reduced surface site.

It was observed (26) that the formation of ¹⁴N¹⁵NO is favoured at higher temperatures. It is possible that elevated temperatures and more reactive surface oxygen lead to the further dissociation of NH₂ groups to NH species (in a process similar to Eq. [1]) which subsequently react with NO to form ¹⁴N¹⁵NO:

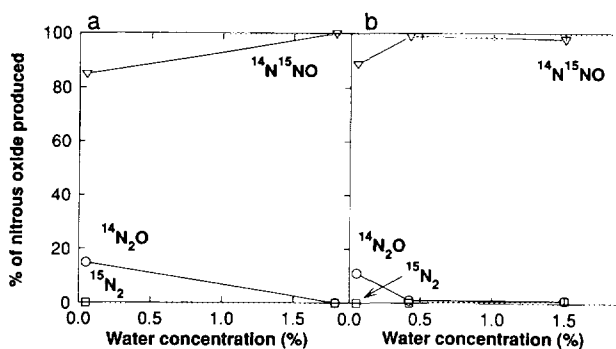
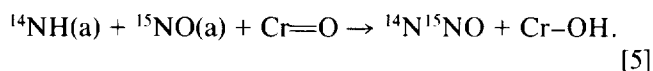
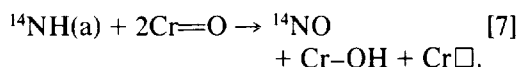
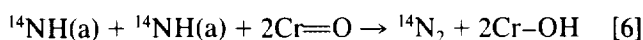
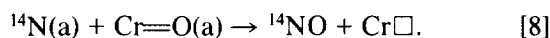


FIG. 4. Internal distribution of the nitrous oxide species as a function of water concentration at 190°C for (a) amorphous and (b) crystalline α -Cr₂O₃ in the presence of 1.8% O₂. (○) ¹⁴N₂O; (▼) ¹⁴N¹⁵NO; (□) ¹⁵N₂O.

Formation of NH groups may also account for the observation of the ammonia oxidation products, $^{14}\text{N}_2$ and ^{14}NO :



Complete dissociation of the NH_3 to a surface $\text{N}(\text{a})$ species is another possible route for ^{14}NO formation:



This model is consistent with the observation that crystalline chromia, which has the more reactive surface oxygen and therefore the greater oxidising (hydrogen abstracting) power (28), has a greater tendency for ammonia oxidation. The model also accounts for the apparent relationship between high selectivities to N_2O and high activities for ammonia oxidation (26).

The effect of H_2O on the product distribution may also be accounted for by the above mechanism. The presence of added water would shift the equilibrium of Eq. [3] to the left, decreasing the number of $\text{Cr}=\text{O}$ groups and vacancies on the surface. The decrease in the concentration of chromyl groups would retard the dissociation of (or the abstraction of hydrogens from) NH_3 , as described in Eq. [1]. In turn, this would account for both the large decrease in $^{14}\text{N}^{15}\text{NO}$ formation (see Eq. [5]) and the reduction in the amount of $^{14}\text{N}_2$ formed over crystalline chromia (see Eq. [6]). Another plausible explanation for the decrease in the reaction rate in the presence of water is that water may compete effectively with ammonia for the active surface sites. Competitive adsorption has previously been used to explain the inhibiting effect of water on the SCR reaction over vanadia-titania catalysts (9).

For the chromia catalysts, significant concentrations of $^{14}\text{N}_2\text{O}$ are only observed when ^{14}NO is also present in the exit gases (26). It was suggested (26) that the $^{14}\text{N}_2\text{O}$ arises from reaction of ^{14}NO , itself formed by reactions [7] or [8], with an ammonia fragment in a way similar to that described in Eq. [5]. The observation that the addition of water completely inhibits the formation of both $^{14}\text{N}_2$ and $^{14}\text{N}_2\text{O}$ is consistent with this proposal.

Effect of Water in the Absence of O_2

Amorphous and $\alpha\text{-Cr}_2\text{O}_3$ catalysts were exposed to alternate wet and dry feed gases under O_2 -free conditions at 280°C . In the absence of oxygen, the reaction between NO and NH_3 has been found to be much slower than that with even small amounts of O_2 (≈ 1000 ppm) over both amorphous and crystalline chromia (26). Consequently,

significantly higher temperatures are required for substantial reaction of NO to occur in the absence of oxygen.

Figure 5 shows the NO and NH_3 conversions and selectivity to N_2O , as a function of time on stream after the addition of $\approx 0.5\%$ and later $\approx 1.5\%$ H_2O . Like the reaction in excess O_2 , the effect of water is reversible. Two other important trends are observed. First, unlike the reaction in the presence of oxygen, the selectivity to N_2O increases with increasing water concentration for both catalysts. Secondly, the addition of $\approx 0.6\%$ H_2O greatly inhibits the reaction, even at 280°C , the effect being particularly pronounced for $\alpha\text{-Cr}_2\text{O}_3$. The effect of water on the activity in the absence of O_2 is much more pronounced than in excess O_2 .

Table 2 shows the effect of water on the products of the reaction between ^{15}NO and $^{14}\text{NH}_3$ over amorphous chromia and $\alpha\text{-Cr}_2\text{O}_3$ in the absence of oxygen. Under

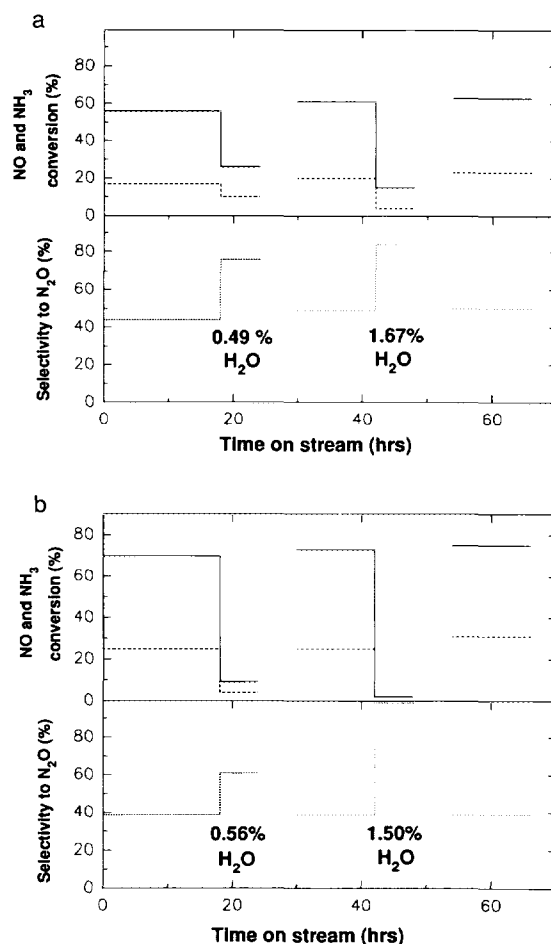


FIG. 5. NO and NH_3 conversions and selectivity to N_2O , as a function of time on stream after being alternately exposed to wet (0.5 and 1.5% H_2O) and dry feed conditions for (a) amorphous chromia and (b) crystalline $\alpha\text{-Cr}_2\text{O}_3$ in the absence of O_2 at 280°C . (solid line) NO conversion; (dashed line) NH_3 conversion; (dotted line) selectivity to N_2O .

these conditions, water affects the product distributions for amorphous and α -Cr₂O₃ in a similar fashion. Figures 6 and 7 show the internal product distributions as a function of water concentration for the nitrogen and nitrous oxide species, respectively. As previously stated, 1.5% water almost completely inhibits the reaction in the absence of oxygen (see Fig. 5). Therefore, only data for 0.05 and ~0.5% water are given in Figs. 6 and 7. These lines are not to be interpreted as indicative of a trend, but merely to illustrate the change in the product distribution with added water. For the nitrogens, the formation of both ¹⁴N₂ and ¹⁵N₂ is completely inhibited when water is added. However, the relative amounts of the nitrous oxide species do not change with added water. Interestingly, while the internal distribution of the nitrous oxide species remains constant, the contribution of the nitrous oxide species (¹⁴N¹⁵NO and ¹⁵N₂O) to the total products increases in the presence of ≈0.5% water (Table 2). Our earlier labelling studies of chromia systems showed that, in the absence of O₂, the two morphologies of chromia exhibit very similar product distributions (26). The dominant form of nitrogen is ¹⁴N¹⁵N, but the nitrous oxide is largely ¹⁵N₂O, and therefore formed by NO decomposition. Additionally, the proportion of both ¹⁴N¹⁵NO and ¹⁵N₂O decreased with reaction temperature, and this was accompanied by a corresponding increase in the amounts of ¹⁴N¹⁵N and ¹⁵N₂, respectively. We suggested (26) that further interaction of the ¹⁴N¹⁵NO and ¹⁵N₂O molecules with the catalyst surface may lead to a loss of oxygen from the nitrous oxide species and the concomitant formation of the respective nitrogens, i.e., ¹⁴N¹⁵N and ¹⁵N₂. The reaction of N₂O and NH₃ in the absence of O₂ was then studied over crystalline chromia, and substantial conversion of N₂O to N₂ was observed along with some conversion of NH₃ to N₂ (26). A two-step process (26) was proposed in which any nitrous oxide species could react with a reduced catalyst surface to form the respective nitrogen, with the adsorbed oxygen released capable

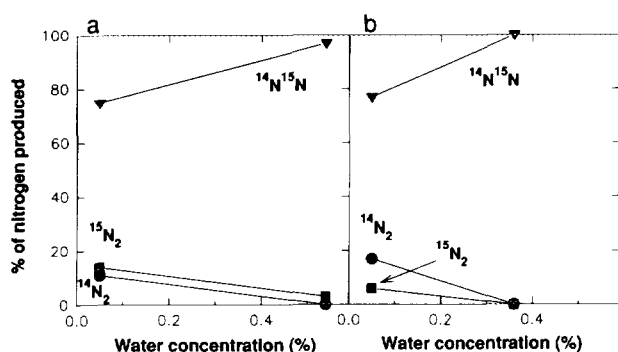


FIG. 6. Internal distribution of the nitrogen species as a function of water concentration at 190°C for (a) amorphous and (b) crystalline α -Cr₂O₃ in the absence of O₂. (●) ¹⁴N₂; (▼) ¹⁴N¹⁵N; (■) ¹⁵N₂.

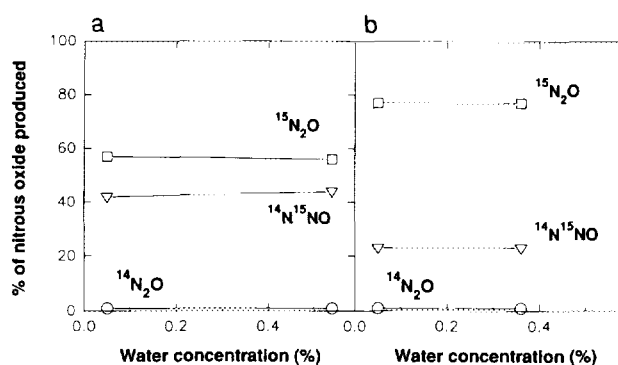
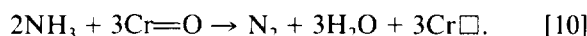
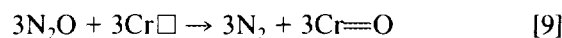
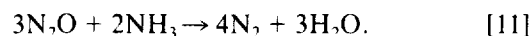


FIG. 7. Internal distribution of the nitrous oxide species as a function of water concentration at 190°C for (a) amorphous and (b) crystalline α -Cr₂O₃ in the absence of O₂. (○) ¹⁴N₂O; (▼) ¹⁴N¹⁵NO; (□) ¹⁵N₂O.

of oxidising NH₃:



The overall reaction was demonstrated (26) to conform to the following stoichiometry:



The present results further support this suggestion. Note that while the addition of water causes an increase in the selectivity to nitrous oxide (made up of ¹⁵N₂O and ¹⁴N¹⁵NO, see Table 2), Fig. 7 shows that the internal distribution of the nitrous oxides remains constant. It is probable that water competes with the N₂O for coordinatively unsaturated reduced chromia sites, preventing further adsorption and conversion of the nitrous oxide species to the corresponding nitrogens, according to Eq. [9].

CONCLUSIONS

(i) In excess (1.8%) oxygen, the addition of 1.5% H₂O decreases NO and NH₃ conversions for all temperatures below about 250°C for both amorphous chromia and α -Cr₂O₃. The effect of water on the activity and selectivity is reversible.

(ii) Water addition completely inhibits the formation of the ammonia oxidation products ¹⁴N₂O and ¹⁴NO over both forms of chromia. For α -Cr₂O₃, the formation of ¹⁴N₂ is also suppressed by the presence of water vapour.

(iii) With O₂ present, increasing amounts of water favour the formation of ¹⁴N¹⁵N relative to that of ¹⁴N¹⁵NO for both amorphous chromia and α -Cr₂O₃.

(iv) In the absence of O₂, the activity and selectivity of both amorphous and α -Cr₂O₃ is markedly affected by the presence of small concentrations (0.5%) of added H₂O, the effect being much more significant than in excess O₂.

(v) For reaction in the absence of O₂, the selectivity to nitrous oxide increases with added water, however, the relative amounts of ¹⁴N¹⁵NO and ¹⁵N₂O remain constant. It is likely that water competes with the nitrous oxide for vacant surface sites, and therefore prevents the conversion of the nitrous oxide species to their respective nitrogens.

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