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The reduction of ${}^{15}N{}^{14}NO$ by CO and by H₂ over Rh/SiO₂: A test of a mechanistic proposal

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ABSTRACT

A literature proposal that the reduction of nitrous oxide by carbon monoxide over rhodium catalysts proceeds by cleavage of the N—N bond has been tested through the use of $^{15}N^{14}NO$ as the reactant. The results disprove the suggestion in that $^{14}N^{15}N$ is the dominant product at temperatures from 336 °C to 356 °C with nitrous oxide conversions from 26% to >99%. Little, if any, $^{14}N_2$ and $^{15}N_2$ is formed, in contrast with the 25% of each expected for the model. Results for the corresponding reaction of $^{15}N^{14}NO$ with H₂ are even more clear-cut in demonstrating the absence of N—N bond cleavage. The activity of the Rh/SiO₂ used here for the N₂O/CO system fell within the rather wide of values reported in the literature for other Rh catalysts. However, activity for the reduction of N₂O by H₂ was approximately five times higher than the only previous result in the literature, that for a Rh/Al₂O₃ catalyst.

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1. Introduction

The formation of N₂O, a potent greenhouse gas, is an undesirable feature of the reduction of NO in automotive catalytic converters containing Pt, Pd or Rh. In tests with simulated exhaust mixtures [1], Rh is the most active metal with N₂O production commencing at temperatures below 200 °C due to the reaction

$$2NO+CO \rightarrow N_2O+CO_2. \tag{1}$$

It starts to disappear above ${\sim}350\,\,^{\circ}\text{C}$ due to the advent of N_2O reduction

$$N_2 O + CO \rightarrow N_2 + CO_2. \tag{2}$$

There have been a number of studies of the kinetics of the latter reaction over rhodium in various forms [2–8]. All agree that the kinetic order in CO is strongly negative and that this is largely compensated by a positive order in N_2O such that the overall order becomes close to zero for stoichiometric mixtures. However, there are some differences between the individual orders obtained and, more particularly, in their interpretation.

The initial study using a supported catalyst, that of McCabe and Wong [3] for Rh/Al₂O₃, reported orders of -1.0 ± 0.15 and $+0.65 \pm 0.1$ for CO and N₂O, respectively. This was interpreted in terms of a model, also adopted for Rh(1 1 1) [4], for Rh foil [2–5] and in Cho's model for the NO + CO reaction over Rh/Al₂O₃ [9–11], in which N₂O was adsorbed weakly and then underwent

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dissociation on a largely CO-covered surface without participation of a vacant site (*), i.e.

$$CO(g) + * \leftrightarrow *CO$$
 (3)

$$N_2O(g) + {}^* \leftrightarrow {}^*N_2O \tag{4}$$

$$^*N_2O \rightarrow N_2(g) + ^*O \tag{5}$$

$$^{*}CO + ^{*}O \rightarrow CO_{2}(g) + 2^{*}.$$
 (6)

Under the assumptions made, this model requires an integral order of +1 for N_2O if the order in CO is -1. McCabe and Wong [3] speculated that the discrepancy between +1 and the +0.65 order they observed experimentally "reflects more complicated precursor kinetics than the simple treatment in our kinetic model".

The non-integral order led Uner [12] to postulate a model in which N_2O , weakly adsorbed according to Eq. (3), dissociated by reversible nitrogen—nitrogen bond cleavage with use of an empty site

$$^{*}N_{2}O + ^{*} \leftrightarrow ^{*}N + ^{*}NO, \tag{7}$$

followed by dissociation of the adsorbed NO

$$^{*}\mathrm{NO} + ^{*} \to ^{*}\mathrm{N} + ^{*}\mathrm{O}, \tag{8}$$

and N₂ formation by dimerization of N adatoms

$$N^* N + N^* N \to N_2(g) + 2^*.$$
 (9)

This model predicts a N_2O order of two-thirds, in line with McCabe and Wong's experimental value, given the assumptions that NO



Research Note

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does not desorb intact, that its dissociation by Eq. (7) is rate limiting and that the surface is largely covered by bridge-bonded CO.

The model of Uner [12] does not seem very reasonable in that the nitrogen—nitrogen bond in gaseous N₂O is much stronger than the nitrogen—oxygen one, 474 kJ/mol versus 161 kJ/mol [13]. Nonetheless, Holles et al. [6] concluded, on the basis of in situ infrared spectroscopy and reaction order data, that the N₂O + CO reaction "appeared to involve N₂O dissociating into N and NO with subsequent dissociation of NO", as per the model of Uner [12]. In particular, they observed the accumulation of NCO species, the formation of which necessarily required cleavage of the N—N bond. Recent DFT calculations have also indicated that cleavage of the nitrogen—nitrogen bond in N₂O is feasible on a Rh(1 1 1) surface, via an intermediate in which N₂O is bound through its terminal atoms, albeit at a rate predicted to be several orders of magnitude slower than that of nitrogen—oxygen cleavage [14].

Kinetic studies subsequent to Uner's proposal have examined other models. Angelides and Tzitzios [7] tested their data for Rh/ Al_2O_3 for conformity to three models – that of McCabe and Wong [3], a modified version in which N₂O dissociation required an adjacent vacant site

$${}^*N_2O + {}^* \to N_2(g) + O^* + {}^*,$$
 (10)

and a standard bimolecular Langmuir–Hinshelwood model in which the rate limiting step was the reaction between adsorbed N_2O and adsorbed CO

$${}^*N_2O + {}^*CO \to N_2(g) + CO_2(g) + 2^*.$$
 (11)

The bimolecular model gave the best fit. However, the most recent study, that of Granger et al. [8], favoured the modified (i.e. adjacentsite requiring) version of the McCabe and Wong model on the basis that the kinetic parameters obtained were in better conformity with those for the NO + CO reaction.

Overall, although the model proposed by Uner [12] does not seem likely, a direct test, as is possible when nitrous oxide containing a single ¹⁵N atom is used, seems worthwhile. If ¹⁵N¹⁴NO is reacted with CO, then, according to the standard McCabe and Wong scheme, the modified version of it and also the bimolecular model of Angelides and Tzitzios [7], ¹⁴N¹⁵N alone should be produced. On the other hand, Uner's scheme implies that product nitrogen arises through random combination of individual nitrogen atoms and hence ¹⁴N₂, ¹⁴N¹⁵N and ¹⁵N₂ should be formed in the statistical ratio 1:2:1. In the present work, we have carried out this experiment and the corresponding one between ¹⁵N¹⁴NO and H₂ where some of the complicating features of the analysis that are present when CO is the reductant are absent.

2. Experimental

The 0.5 wt% Rh/SiO₂ sample was made by impregnation of silica gel (Davison grade 62, BET surface area of $285 \text{ m}^2/\text{g}$, particle size 180 to $210 \mu\text{m}$), with a solution of RhCl₃. The dispersion was 38% as measured by H₂ chemisorption following overnight drying at 140 °C and reduction in 10% H₂/He on a ramp (at 1 °C/min) ending with 2 h at 350 °C.

Catalytic measurements were carried out in a flow system described in detail previously [15]. In essence, the reactant stream (nominally 2000 ppm N₂O, 2000 ppm CO or H₂, balance He with total flow rate of 100 cm³ (STP)/min) was passed down-flow over 75 mg of the Rh/SiO₂ supported between quartz wool plugs in a Pyrex reactor with an internal diameter of 6 mm. The sample of Rh/SiO₂ had been used previously in studies involving reactions of mixtures of NO, CO and H₂ [15] during which it exhibited constant activity if flushed with He overnight between runs and the same procedure was followed here.

The stream leaving the reactor was analysed on-line in three ways – by quadrupole mass spectrometry (Balzers Thermostar model GSD 300T) every 20 s, by gas chromatography (MTI model M200 with molecular sieve and Poraplot U columns) every 3 min during isotopic substitution and by FTIR spectroscopy (Nicolet Magna 550 fitted with a 16 cm flow-through cell) accumulating 64 scans at 0.25 cm⁻¹ resolution every 10 min. The infrared spectra were processed to obtain outlet concentrations using the program, MALT, developed by Griffith [16] and, in the case of the isotopomers of N₂O, using a database attributable to Toth [17].

The ¹⁵N¹⁴NO was obtained from Cambridge Isotope Laboratories with the chemical and isotopic purity each stated to be >98%. Mass spectrometric analysis over the parent ion region showed 1.0% ¹⁴N₂O and 0.4% ¹⁵N₂O, with the balance nitrous oxide containing a single ¹⁵N. FTIR analysis showed that the latter was >95% ¹⁵N¹⁴NO with ¹⁴N¹⁵NO below the detection limit of 5%. Unlabelled and labelled nitrous oxides were each made up as ~5% mixtures in helium and supplied from separate electronic mass controllers with the two streams interchanged using a low volume four-port valve (Valco Inst., 1/16″). The streams were run in turn for 20 min each with the changeover between them completed by the second subsequent cycle of the mass spectrometer (~40 s).

3. Results and discussion

3.1. The reduction of N₂O by CO

The lines in Fig. 1 show the course of the $^{14}N_2O + CO$ reaction over the Rh/SiO₂ catalyst when ramped up at 2 °C/min. Conversions (*X*) were calculated from the concentrations (*C*) of nitrous oxide and carbon dioxide using the relationships

$$X_{\rm N2O} = 100^{*} [C_{\rm N2O}(in) - C_{\rm N2O}(out)] / C_{\rm N2O}(in)$$
(12)

and

$$X_{\rm CO} = 100^* C_{\rm CO2}(\rm out) / C_{\rm CO}(\rm in).$$
(13)

The concentration of nitrous oxide was monitored using the signal from its fragment ion at m/z = 30 ($^{14}N^{16}O^+$) and that of carbon



Fig. 1. Conversions versus temperature for the reaction of 1927 ppm N₂O with 1980 ppm CO over 75 mg of 0.5 wt% Rh/SiO₂. The continuous curves are calculated from the MS data for the reaction of ¹⁴N₂O when the temperature of the catalyst was ramped up at 2 °C/min. Symbols are for subsequent reaction at the fixed temperatures used for the runs with ¹⁵N¹⁴NO. The inset plot shows an Arrhenius plot for turnover frequencies over the conversion range from 5% to 20% during the ramp-up.

dioxide from the signal at m/z = 22 attributable to the doubly charged CO₂⁺⁺ ion alone. The signals of the parent ions could not be used as the resolution of the mass spectrometer was insufficient to resolve ¹⁴N₂ from ¹²C¹⁶O (both at m/z = 28) or ¹⁴N₂¹⁶O from ¹²C¹⁶O₂ (both at m/z = 44).

Table 1 compares the activity of the Rh/SiO₂ catalyst with literature data for other catalysts in terms of turnover frequency (TOF) expressed as molecules N₂O per surface rhodium atom per second. The range of experimental conditions in the studies was quite large and the activities reported by the authors have been converted to a mid-point temperature (340 °C) and the concentrations used here using the values given for activation energies and kinetic orders. The present results are reasonably close to those in the original study by Wong and McCabe [3] in terms of both activity and activation energy. However, the activity was much below that of Belton and Schmieg [4] for a Rh(1 1 1) surface and also that of Granger et al. [8] for a very highly dispersed Rh/Al₂O₃ catalyst.

Experiments using ${}^{15}N^{14}NO$ in place of ${}^{14}N_2O$ were carried out subsequent to completion of the ramp at four temperatures in the sequence 1–4 as shown in Fig. 1. The conversions determined by gas chromatography (gc) and FTIR spectroscopy (FT) were in good agreement and close to those measured by mass spectrometry during the initial ramp-up with ${}^{14}N_2O$. FTIR spectra of the unreacted nitrous oxide from the experiments at the three lowest temperatures (not shown) did not show any ${}^{14}N^{15}NO$ (i.e. <5% as in the starting material), thus excluding isomerization of ${}^{15}N^{14}NO$.

The calculation of the distribution between the three isotopic nitrogen product species from the mass spectrometer signals with m/z = 28, 29 and 30 required accurate correction for the contributions from several interfering species. The most significant corrections were the contributions from fragmentation of unreacted ¹⁵N¹⁴NO to the signals at m/z = 29 and 30 and for the combined contributions of unreacted carbon monoxide and fragmentation of carbon dioxide (yielding ¹²C¹⁶O⁺) to the signal at m/z = 28. The allowance for unreacted carbon monoxide included correction for the contribution of natural abundance ¹³C¹⁶O to the signal at m/z = 29 and of natural abundance ¹³C¹⁶O to the signal at m/z = 29 and of natural abundance ¹³C¹⁸O to m/z = 30. The former correction was always insignificant but the latter became significant when carbon monoxide conversions were low.

Bypass analyses showed that the ${}^{15}N^{14}N^{16}O$ used here fragmented to yield ions with m/z = 28, 29, 30 and 31 for which the intensities were 0.6%, 19%, 42% and 4%, respectively, of the intensity of the parent ion at m/z = 45. This pattern was qualitatively in good agreement with the data of Begun and Landau [18] in showing a minor extent of interchange between ${}^{15}N$ and ${}^{14}N$ during the course of fragmentation. However, the extent of fragmentation to the ions at 29 and 30 in the present work was approximately twice as great as they found, presumably due mass spectrometer differences (quadrupole here versus the magnetic sector instrument used in their study).

Table 2 shows the raw ion currents observed in the four isotopic substitution experiments, the corresponding signals after correction (in parentheses) and the distribution amongst the nitrogen species derived from the latter. As may be seen, the magnitude of the corrections to the signals at m/z = 28 and 30 was very large, >95% of the raw signals in some cases. The uncertainties shown for the distributions are calculated on the basis of an estimated ±3% error in each of the systematic corrections applied to the raw signals. The estimate for ¹⁴N₂ includes an additional uncertainty, allowed for to the extent shown in the footnote, to account for a noticeable drift in the background during the course of the measurements.

The model of Uner predicts that the nitrogen produced by the reduction of ¹⁵N¹⁴NO by CO should comprise ¹⁴N₂, ¹⁴N¹⁵N and ¹⁵N₂ in the ratio 1:2:1 given the random combination of nitrogen adatoms implied by reaction Eq. (8) Despite the magnitude of the corrections required, it is clear from the data in Table 2 that the amounts of ¹⁴N₂ and ¹⁵N₂ formed, if any, were very small relative to that of ¹⁴N¹⁵N. In particular, the amount of ¹⁵N₂ formed was certainly <1% based on the most accurate measurement, that at 356 °C when the conversion of nitrous oxide was >99% and the correction for its fragmentation very small. Thus, reaction according to the model proposed by Uner [12] is ruled out. On the other hand, the exclusive production of ¹⁴N¹⁵N is in accord with the other mechanistic models in the literature.

3.2. The reduction of nitrous oxide by hydrogen

A similar set of experiments was carried out for the reduction of nitrous oxide by hydrogen (Fig. 2). Here, it was possible to follow,

Table 1

Activation energies and turnover frequencies for the reaction of N₂O with CO.

Reference	Sample	D _{Rh} (%)	% in feed		E _a (kJ/mol)	Kinetic order		TOF (s ⁻¹) at 340 $^\circ C^a$	
			N ₂ O	СО		N ₂ O	CO		
McCabe and Wong [3]	0.5% Rh/Al ₂ O ₃	33	1.0	1.1	169	0.65	-1	0.022	
Belton and Schmieg [4]	Rh(111)	-	0.5	0.5	167	1.14	-1.18	0.40	
Holles et al. [6]	1.85% Rh/Al ₂ O ₃	40	4.0	4.0	109	0.72	-0.86	0.061	
Granger et al. [8]	0.2% Rh/Al ₂ O ₃	93	0.6	0.6	137	0.75	-0.54	0.50	
This work	0.5% Rh/SiO2	38	0.2	0.2	175	nd	nd	0.030	

nd: not determined.

^a Interpolated at, or extrapolated to, 340 °C and the feed composition used in this work based on the activation energies and the kinetic orders reported by the authors.

Table 2

Distribution of isotopic N₂ species for the reaction of ¹⁵N¹⁴NO with CO over Rh/SiO₂.

Temperature (°C)	N ₂ O (CO) conversions (%)	$10^{10} imes$ Ion current ^a (amps)			Distribution ^b (%)		
		28	29	30	$^{14}N_{2}$	$^{14}N^{15}N$	¹⁵ N ₂
356	99.2 (96.1)	752 (-16)	5534 (5526)	52 (32)	-0.3 ± 0.6	Balance	0.6 ± 0.1
346	52 (49)	3657 (-91)	2982 (2760)	532 (28)	-3 ± 4	Balance	1.0 ± 0.5
336	26 (23)	5204 (-121)	1664 (1328)	779 (19)	-9 ± 12	Balance	1.4 ± 1.5
350	64 (62)	2931 (10)	3618 (3447)	416 (29)	0.3 ± 3	Balance	0.8 ± 0.3

^a Raw signals with signals after adjustment for contributions from other species in parenthesis.

^b The errors shown correspond to an estimated uncertainty of $\pm 3\%$ in each adjustment for other species and, in the case on $^{14}N_2$, an absolute uncertainty of 10×10^{-10} amps in the background signal at m/z = 28 (see text).

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Fig. 2. Conversions versus temperature for the reaction of nominally 2036 ppm N₂O with 2076 ppm H₂ over 75 mg of 0.5 wt% Rh/SiO₂. The continuous curves are calculated from MS data for the reaction of $^{14}N_2O$ when the temperature of the catalysts was ramped up at 2 °C/min. Symbols are for subsequent reaction at the fixed temperatures used for the runs with $^{15}N^{14}NO$. The inset plot shows an Arrhenius plot for the apparent first order rate constant (see text) over the conversion range 7–80% during the ramp-up.

with varying degrees of accuracy, the concentrations of all four chemical species in the ${}^{14}N_2O + H_2$ reaction system by mass spectrometry. Nitrous oxide could be monitored in two ways (using the signals due to the parent ion at m/z = 44 and the fragment ion at 30). Likewise, water could be followed in two ways (m/z = 17 and 18). The least accurate determinations were for N₂ (due to the drift in the background signal at m/z = 28 arising from CO produced by reactions involving carbon on the tungsten source filament) and water (due to adsorption on the silica support).

All measurements showed that conversions were significant (~5%) at 30 °C and rose with temperature to a maximum of 90% at 130 °C with a slight fall and then rise again at higher temperatures. Two isotope substitution experiments were carried out subsequently, at 114 °C and 72 °C, where the conversions were below those during the initial ramp-up. Despite the deactivation, the conversions observed here were much greater than those expected from the only previous study of the N₂O + H₂ reaction over supported rhodium, that of Miyamoto et al. [19] for a 0.5 wt% Rh/Al₂O₃ catalyst with a dispersion of ~49%. In terms of turnover frequency, the Rh/SiO₂ here exhibited a value of 0.022 s⁻¹ during the second isotope experiment at 72 °C versus 0.0044 s⁻¹ calculated from the parameters of the kinetic model proposed in their work, i.e.

$$N_2 O(g) + {}^* \to N_2(g) + O^* \tag{14}$$

$$H_2(g) + O^* \to H_2O(g) + {}^*. \eqno(15)$$

The rate expression for this model is

$$Rate = k_1 k_2 C_{N20} C_{H2} / (k_1 C_{N20} + k_2 C_{H2}).$$
(16)

The dashed line in Fig. 2 showing the conversions predicted by this model was obtained assuming integral reactor behaviour. Eq. (16) was integrated exactly and the resultant expression solved at a closely spaced set of temperatures using a simple iterative method.

With $C_{N20}=C_{H2}$ (= C_i), as close to true in the experiments here, Eq. (16) reduces to the first order expression

Rate =
$$k_{app}C_i$$
 where $k_{app} = k_1 k_2 / (k_1 + k_2)$. (17)

The dashed line in the inset plot on Fig. 2 shows an Arrhenius plot for k_{app} calculated directly from the k_1 and k_2 given by Miyamoto et al. [19]. The points in the inset plot were calculated from our experimental data using an equation with the standard form for integral first order behaviour

$$k_{\rm app}F/A = -\ln(1-X) \tag{18}$$

where *X* is the fraction conversion and *F* (the gas flow rate) and *A* (the surface area of Rh) bring the units for k_{app} in line with the cm/s units used by Miyamoto et al. [19]. The conversion range is 7–80%, with higher conversion data excluded to avoid a potential departure from first order behaviour as the assumption that H₂ and N₂O concentrations are exactly equal starts to break down. The best-fit slope to the points corresponds to an activation energy for k_{app} of 45 kJ/mol, in close agreement with that expected for the model of Miyamoto et al. [19] for the same temperature range, namely 49 kJ/mol at 40 °C falling to 43 kJ/mol at 100 °C.

Table 3 shows the analytical data for the two isotope experiments. In the absence of CO and CO₂, corrections to the signal at m/z = 28 were much smaller than necessary for the data for the N₂O + CO reaction in Table 2. This reduced the uncertainty in the determination of ¹⁴N₂ despite a greater drift in the baseline at m/z = 28. However, the determination of ¹⁵N₂ was somewhat less certain as the extent of fragmentation of ¹⁵N¹⁴N¹⁶O to ¹⁴N¹⁶O⁺ within the mass spectrometer in this experiment was slightly different from that in the run with CO, 38% versus 42%, and was established less accurately.

The results in Table 3 are even more clear-cut than those in Table 2 for the corresponding reaction using carbon monoxide – formation of both $^{14}N_2$ and $^{15}N_2$ was negligible compared with that of $^{14}N^{15}N$. The most accurate determination of the minor species, that of $^{15}N_2$ at 114 °C, is <0.5%. Thus, as with data for the reaction of $^{15}N^{14}NO$ with CO, there was no detectable cleavage of the N–N bond.

Table 3

Distribution of isotopic N₂ species for the reaction of ¹⁵N¹⁴NO with H₂ over Rh/SiO₂.

Temperature (°C)	N ₂ O (H ₂) conversion (%)	$10^{10} \times \text{lon current}^{a} \text{ (amps)}$			Distribution ^b (%)			
		28	29	30	¹⁴ N ₂	¹⁴ N ¹⁵ N	¹⁵ N ₂	
114	72 (71)	117 (76)	3811 (3675)	292 (12)	2 ± 1	Balance	0.3 ± 0.4	
72	23 (21)	55 (6)	1197 (843)	718 (-6)	1 ± 4	Balance	-1 ± 3	

^a Raw signals with signals after adjustment for contributions from other species in parenthesis.

^b The errors shown correspond to an estimated uncertainty of $\pm 5\%$ in each adjustment for the extraneous signals from species other than nitrogen and, in the case of $^{14}N_2$, an uncertainty of 40×10^{-10} amps in the background signal at m/z = 28.

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4. Conclusions

The present results show that ¹⁴N¹⁵N is the exclusive product of the reduction of ¹⁵N¹⁴NO by CO over supported rhodium with very little, if any, formation of ${}^{14}N_2$ and ${}^{15}N_2$. This rule against a literature mechanism that postulates reaction via an initial cleavage of the nitrogen-nitrogen bond in nitrous oxide. Isotopic analysis of the corresponding reaction with H_2 as the reductant likewise shows a clean reaction by cleavage of the N–O bond alone. The Rh/SiO_2 used here was much more active for the $N_2O + H_2$ reaction than previously reported for a Rh/Al₂O₃ catalyst with similar dispersion, but its activity for the N₂O + CO reaction was within the rather wide range of values in the literature.

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