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Evidence for an N_2O intermediate in the catalytic reduction of NO to N_2 on rhodium surfaces

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Abstract

Rates for isotopically labelled molecular nitrogen production during the isothermal steady-state reduction of NO to N_2 by CO on Rh(1 1 1) surfaces were measured by using a molecular beam technique. The replacement of surface ^{14}N by ^{15}N upon switching the isotopic nitrogen label in the NO (from ^{14}NO to ^{15}NO) was determined to occur via the exclusive formation of $^{14}N^{15}N$; no $^{14}N^{14}N$ was detected in these experiments. This result provides direct kinetic evidence for a mechanism for molecular nitrogen production involving the formation of an N–NO intermediate. The implications for the design of catalytic converters are briefly discussed.

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1. Introduction

Metallic rhodium has proven to be one of the best catalysts for the conversion of NO_x to molecular nitrogen, a critical step in pollution-control processes [1,2]. Its great expense, however, makes the identification of other alternatives highly desirable. It has been thought that the key property of any viable catalyst for NO_x reduction is its ability to break the N–O bonds of the reactants [3–16]. Since, according to this mechanism, the resulting surface nitrogen atoms recombine rapidly to produce N_2, it could be concluded that the formation of N_2O, an undesirable side product which requires the formation of a bond between one nitrogen atom and molecular NO, could be minimized kinetically by maintaining a low NO concentration in the reaction mixture [7]. However, kinetic evidence is provided in this communication for the formation of an N–NO surface intermediate during the production of molecular nitrogen as well. This implies that it may not be possible to control the selectivity for N_2 versus N_2O production by changing the composition of the reactant gas, and that catalysts with particularly high activity towards N_2O dissociation may be needed instead.

2. Experimental

The isothermal kinetic experiments reported here were performed by using a variation of the molecular beam method originally developed by King and Wells [17–19]. A Rh(1 1 1) single-crystal surface is exposed to mixed NO + CO collimated effusive beams while the temporal evolution of the rates for both the consumption of the reactants (CO, NO) and the appearance of the products (CO_2, N_2, N_2O) are followed by mass spectrometry.

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The experimental apparatus, described in detail elsewhere [20], consists of a stainless-steel ultra-high vacuum (UHV) vessel pumped to a base pressure below 2×10^{-10} Torr and equipped with a computer-controlled mass quadrupole placed in the back of the chamber and pointing away from the sample in order to integrate any angular dependence of the molecules desorbing from the surface. A collimated multi-channel micro-capillary array doser 1.2 cm in diameter is used for directional exposure of the sample to the reactants, a sputtering ion gun for sample cleaning, and a crystal holder for three-dimensional translation and on-axis rotation as well as for resistive heating and liquid nitrogen cooling.

The Rh(1 1 1) single-crystal (a 1.10×0.56 cm^2 rectangle) was prepared in the usual manner, and cleaned in situ, initially by Ar^+ sputtering and before each experiment by cycles of oxygen exposures (1×10^{-7} Torr at 900 K for up to 20 min) and annealing to 1200 K until the NO TPD spectra reported in the literature [21] could be reproduced. The total flux of the beam was fixed at 0.5 monolayers per second (ML/s), and the distance between the doser and the sample was set to 1.0 cm in order to ensure the homogeneity of the beam profile across the surface for reliable kinetic measurements [22]; only the central 20% of the beam was intercepted by the rhodium crystal in this arrangement [20]. A flag was used to intercept the beam at will. The surface temperature was monitored continuously with a chromel–alumel thermocouple spot-welded to the back of the crystal, and kept constant during the kinetic runs with a home-made precision temperature controller. Isotopically labelled ^{15}NO (CIL, 98% ^{15}N purity) and ^{13}CO (CIL, 99% ^{13}C purity) and regular ^{14}NO and ^{12}CO (Matheson, 99.9% purity) were used as supplied.

3. Results and discussion

The methodology used in the kinetic NO + CO/Rh(1 1 1) isothermal runs reported here has been described in detail elsewhere [23], but is briefly reviewed below with the example displayed in Fig. 1 in order to help understand the data in Figs. 2 and 3. In these runs the clean rhodium surface is heated to a fixed reaction temperature ($T = 480$ K), and first exposed to a (1:1) premixed $^{14}NO + ^{12}CO$ beam for a period of time sufficiently long (210 s) to reach the appropriate steady-state catalytic condition. The sequence of events in this first phase of the kinetic run is as follows: (1) the mass spectrometer is set to follow the partial pressures of the gases of interest (^{12}CO, ^{14}NO, ^{15}NO, $^{12}CO_2$, $^{14}N^{14}N$, $^{14}N^{15}N$, $^{15}N^{15}N$) continuously over time as the changes described below take place; (2) the $^{14}NO + ^{12}CO$ molecular beam is turned on at time $t = 10$ s while keeping the flag in the intercepting position so that the crystal is not yet exposed directly to the beam. This leads to respective increases in the partial pressures of the reactants to new steady-state values; (3) at approximately $t = 20$ s, the flag is removed from the path of the beam to allow for its direct impingement on the surface. This causes a transient change where both decreases in the partial pressures of the reactants and increases in the signals of the products are seen before all pressures reach the new steady-state levels associated with the $^{14}NO + ^{12}CO$ catalytic conversion [16]; (4) during the steady-state regime the molecular beam is deliberately blocked for a short period of time by raising and lowering the flag (at times $t = 160$ and 185 s, respectively, in this example) to check on the values of the steady-state reaction rates; and (5) the molecular beam is eventually turned off to stop the reaction (at about $t = 220$ s in Fig. 1).

At this point, a steady-state coverage of strongly bonded atomic nitrogen ($\Theta_N \sim 0.17$ ML) is present on the surface [16,23]. The original $^{14}NO + ^{12}CO$ beam is then rapidly replaced by an identical beam with either $^{15}NO + ^{13}CO$ or $^{15}NO + ^{12}CO$, and a second kinetic run is started immediately afterwards. The data for this second run (with a 1:1 $^{15}NO + ^{12}CO$ mixture in this example) are displayed in the 250–450 s time range of Fig. 1. Finally, steady-state rates are measured again by blocking and unblocking of the beam (at $t = 365$ and 385 s, respectively, in Fig. 1).

Fig. 2 provides a closer look at the temporal evolution of the mass-spectrometer signals for the different isotopomers of molecular nitrogen ($^{14}N^{14}N$, $^{14}N^{15}N$, and $^{15}N^{15}N$) produced in the

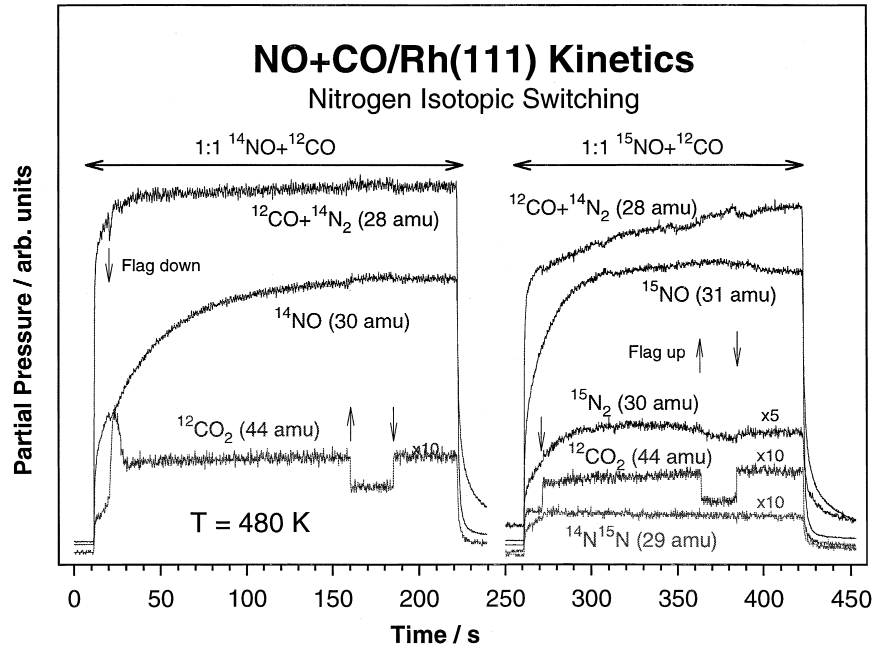

Fig. 1. Typical raw data obtained from the isotope switching experiments discussed in this letter. The first 220 s of the experiments were performed in the same way as in the previously reported kinetic runs [15] in this case by using a 1:1 $^{14}NO + ^{12}CO$ mixture and $T_{reaction} = 480$ K. After that, the beam was shut off and replaced with a mixture of $^{15}NO + ^{12}CO$ ($t = 250$–450 s), and the reaction was run for an additional $\Delta t = 150$ s before stopping it again. Blocking and unblocking of the beam (at $t = 365$ and 385 s in this example, respectively) was performed in order to measure the reaction rates directly associated with the molecular beam.

second phase of the experiment. This figure again displays the raw kinetic data, only the time scale is now shifted so $t = 0$ s corresponds to the time at which the second beam is turned on. In this example, the beam is unblocked at $t = 5$ s to allow for its direct impingement on the rhodium surface (first flag down point), and blocked after a specific period of time Δt (10 s – the flag up point – in the example illustrated in Fig. 2) in order to determine the reaction rates directly connected with the impingement of the beam on the surface (which are proportional to the drops in pressure seen when blocking the beam).

It should be mentioned at this point that there are a number of difficulties associated with these experiments because of the interference of background gases in the measurements and because of the overlap of signals from different compounds in the mass spectrometer. The latter problem was addressed here by using different isotopic substitutions. For instance, two sets of identical experiments, with ^{12}CO and ^{13}CO, were performed in the studies shown in Fig. 2 in order to separate the overlapping signals from ^{12}CO and $^{14}N^{14}N$ at 28 amu and from ^{13}CO and $^{14}N^{15}N$ at 29 amu in the mass spectrometer, and thus discriminate between the evolution of the partial pressures of nitrogen and carbon monoxide. Reproducibility between the two sets was checked by comparison of the rates for ^{15} $N^{13}N$ (30 amu) production measured in both cases, and independently by following the rates of carbon dioxide formation (see figure).

Additional experiments were required to assess the contribution of background ^{12}CO to the 28 amu signal in the mass spectrometer. This was particularly important because changes in the raw 28 amu traces were sometimes seen in the early part of the kinetic runs, allegedly because of the displacement of ^{12}CO from the walls of the chamber by the gases in the beam. The results from a number of independent experiments allowed us to dispose of this interference. For

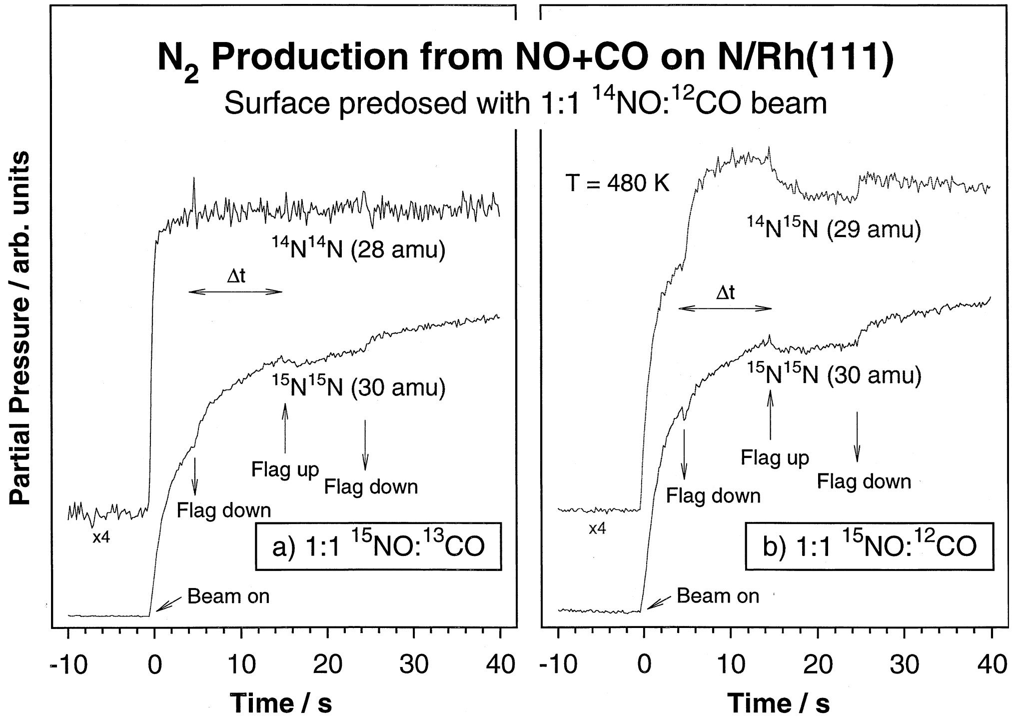

Fig. 2. Raw data from the second half of the isotope switching experiments described in Fig. 1 ($T = 480$ K, NO:CO = 1:1). The first 250 s of the kinetic runs (the first half, not shown here) were carried out by using a $^{14}NO + ^{12}CO$ beam, as reported before [15,23]. This beam was then replaced with a similar mixture of either $^{15}NO + ^{13}CO$ (left) or $^{15}NO + ^{12}CO$ (right). The steady-state rates for the formation of the three possible N_2 isotopomers as a function of the time delay (Δt) after the isotope switching is indicated by the pressure drop at the first flag-up point, $t = 15$ s in this case. While changes in the rates for $^{14}N^{15}N$ and $^{15}N^{15}N$ production are easily observed, no $^{14}N^{14}N$ formation is observed at all.

instance, it was determined that blocking and unblocking of the beam during the pressure changes mentioned above results in absolutely no change in the 28 amu mass-spectrometer signal. This indicates that the observed phenomenon is not related to the direct impingement of the beam on the surface. In addition, the same problem (an early increase in the 28 amu signal) was also seen when both halves of the experiment were carried out with ^{15}NO, in which case no $^{14}N_2$ should be produced. The important point is that the reaction rates reported in this letter were calculated by measuring differences in partial pressure between unblocked and blocked beam conditions. This difference corresponds directly to rates from conversion of the molecules in the beam, independently of any other signals due to the background.

One of the most important things to notice from the data in Fig. 2 is that while the signals for $^{14}N^{15}N$ and $^{15}N^{15}N$ change significantly upon interception of the beam at $t = 15$ s, that for $^{14}N^{14}N$ does not. This provides direct indication for the exclusive production of $^{14}N^{15}N$ and $^{15}N^{15}N$ in these experiments. Put another way, the molecular nitrogen produced by exposing the ^{14}N-covered Rh(1 1 1) to $^{15}NO + CO$ beams always contains at least one ^{15}N atom. This is seen more clearly in Fig. 3, which displays the steady-state rates of formation for all three isotopically substituted nitrogen molecules as a function of the time Δt the ^{14}N-covered surface is exposed to the $^{15}NO + CO$ beams. Again, it is apparent from these data that the adsorbed ^{14}N is removed exclusively as $^{14}N^{15}N$, and that no detectable $^{14}N^{14}N$ is produced at any time during this second stage of the experiment

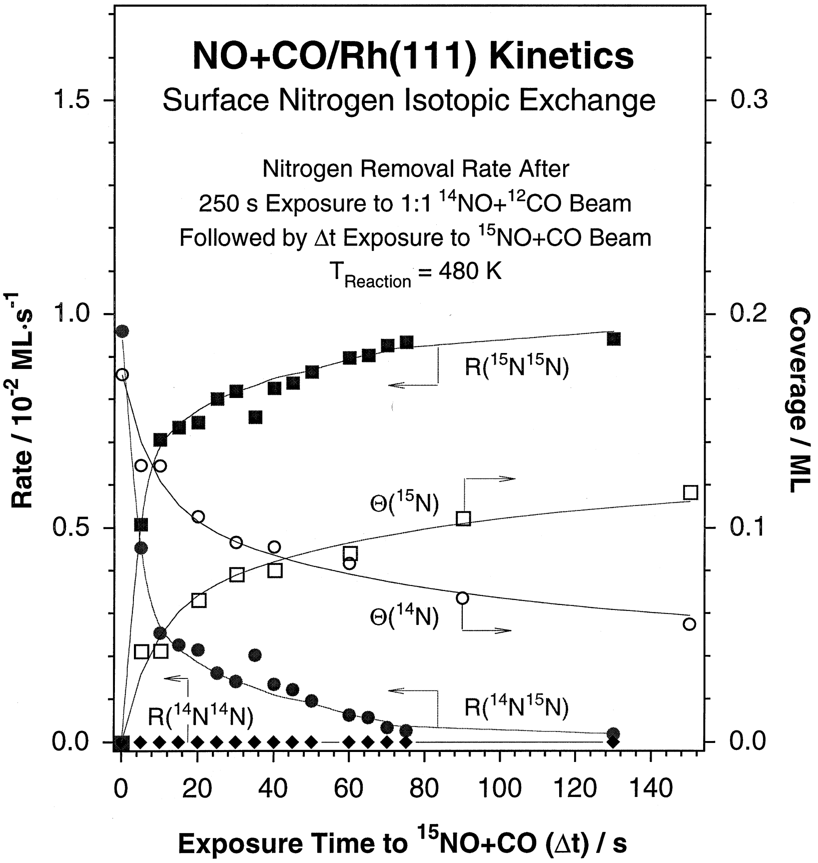

Fig. 3. Evolution of the $^{14}N^{14}N$, $^{14}N^{15}N$, and $^{15}N^{15}N$ production rates (filled symbols), and of the ^{14}N and ^{15}N surface coverages (hollow symbols), during the steady-state reduction of NO with CO on Rh(1 1 1) as a function of the time Δt the ^{14}N-covered surface is exposed to a $^{15}NO + CO$ beam. The original ^{14}N is slowly replaced by new ^{15}N, but only via the formation of $^{14}N^{15}N$ (no $^{14}N^{14}N$ is ever detected). This implies that molecular nitrogen must be produced via the formation of an N–NO intermediate.

(with the ^{15}NO-containing beams). Notice that this is so even in the early part of the kinetic runs, when the surface nitrogen is mostly ^{14}N (for $\Delta t < 50$ s, see the time evolution of the steady-state nitrogen coverages also plotted in Fig. 3 [16,23]). Independent corroboration of our conclusion was obtained by additional experiments with different $^{14}NO + {}^{15}NO + CO$ mixtures, the data from which indicated that the rate of $^{14}N^{14}N$ production at early Δt's is directly proportional to the amount of ^{14}NO in the beams [24]. The implication from these results is straightforward: the production of molecular nitrogen on rhodium under steady-state catalytic conditions must involve an undissociated nitrogen monoxide molecule. The most likely way this may happen is via the formation and subsequent decomposition of an N–NO surface intermediate. This contradicts the previously held idea that production takes place via the recombination of two nitrogen atoms on the surface [14].

Our conclusion has profound implications for the mechanism of catalytic NO reduction processes. As indicated in the introduction, the production of N_2 via an N–NO intermediate argues against N_2 and N_2O originating from parallel mechanisms [14], and precludes the possibility of tuning the selectivity of NO reduction via changes in the NO surface concentration. It is important to point out that the $N + N \rightarrow N_2$ reaction is in fact feasible on Rh(1 1 1) [25,26], and that at low temperatures ($T < 500$ K) N_2 formation from NO does not appear to involve a direct N–NO interaction. What our results indicate is that atomic nitrogen recombination is not the dominant step in nitrogen production during the catalytic reduction of NO [15,23]. Importantly, results from high-pressure catalytic studies on the reduction of NO with CO over Rh(1 1 1) have shown no significant dependence of the N_2/N_2O yield ratio on either NO or CO partial pressures or temperature over a wide range of conditions [27]. This is what would be expected if the formation of both products involves a common intermediate, as stipulated here.

Acknowledgements

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