Surface intermediates during the catalytic reduction of NO on rhodium catalysts: a kinetic inference

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Abstract

Isothermal kinetic studies on the reduction of NO by CO on Rh(1 1 1) single-crystal surfaces, performed under vacuum by using collimated effusive molecular beams, have provided information on the coverages and nature of the surface intermediates involved in that reaction under catalytic conditions. Three major conclusions were reached. First, the optimum rate of reaction is achieved when the steady-state coverages of NO and CO on the surface reach the 1:1 stoichiometric ratio. The surface coverages are controlled by a synergistic balance between the composition of the gas and the surface temperature: higher temperatures tend to require higher CO:NO ratios. Second, under optimum conditions the surface of the catalyst is mostly covered with atomic nitrogen. This nitrogen appears to cluster in islands, and further conversion to molecular nitrogen takes place preferentially at their periphery. Finally, the formation of molecular nitrogen under catalytic conditions is likely to involve the formation of a N–NO intermediate. Evidence for these conclusions is provided. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Metallic rhodium has proven to be one of the best catalyst 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; the resulting surface nitrogen atoms are believed to then recombine rapidly to N_2 [3–14]. According to this mechanism, the formation of N_2O, an undesirable side product which requires the forma-

tion of a bond between one nitrogen atom and a NO molecule, could be minimized kinetically by maintaining a low NO concentration in the reaction mixture [7]. This idea is challenged below.

The reaction of NO with CO on rhodium surfaces has been studied in some detail under vacuum [3–23]. On Rh(1 1 1), early temperature programmed desorption (TPD) experiments proved that the conversion of NO with CO takes place even under vacuum [17,18]. It was also soon found that the key in understanding the details of this reaction lies in the elucidation of the mechanism for the conversion of NO to N_2 on the surface. Interestingly, the desorption of molecular nitrogen from NO decomposition on Rh(1 1 1) occurs in two stages, around 470 and above 500 K [17,19,24–27]. Particularly puzzling is the fact that the first TPD N_2 peak at 470 K does not shift in

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temperature with changing coverages, a behavior generally associated with first-order processes. Nevertheless, experiments with different surface-sensitive techniques [24–27] have shown that NO dissociation occurs at quite low temperatures, below 300 K at low coverages and around 450 K at high coverages. This strongly suggest that the catalytic reduction of NO is determined by the mechanism by which N_2 is formed on the surface.

Additional clues on the microscopic details of NO conversion processes come from studies carried out at moderate pressures [6,7,12,28]. It is worth mentioning here that even though the commercial Rh/Al_2O_3 automotive catalysts produce N_2 exclusively over a wide range of operating conditions [13,21,22], the production of some N_2O was detected in the atmospheric-pressure single-crystal studies [7]. Fisher and co-workers [4,5,17,18,20,26], in their initial studies in the mid-eighties, proposed two separate pathways for this, the generally accepted recombination of nitrogen atoms on the surface, and a disproportionation between adsorbed NO and N which could also account for the formation of the N_2O. Newer experimental data by Belton and co-workers [6,7,12,28,29] argued that the latter does in fact not occur on Rh(1 1 1), at least under vacuum. Nevertheless, questions on the nature of the rate-limiting step and of the source for N_2O production are still open to debate. Our experimental data support the idea of the formation of N_2O intermediates during the production of molecular nitrogen.

2. Experimental

The experimental procedure used here for rate determinations in the NO+CO/Rh(1 1 1) system is based on exposing the clean rhodium surface to a molecular beam with a specific premixed ratio of NO and CO and on following the partial pressure of the different gases of interest by mass spectrometry as a function of time [30–33]. Our methodology is exemplified in Fig. 1, which shows raw kinetic data for the evolution of the partial pressures of N_2, N_2O (not detected ever in these experiments), NO, CO and CO_2 over time for the case of a 1:1 NO:CO ratio and a reaction temperature of 475 K. A series of actions are taken during these experiments, as follows: (1) at time $t = 10$ s the NO + CO molecular beam is turned on with the flag in the intercepting position so the crystal is not yet exposed directly to the beam. At this point the reactants (NO and CO) are scattered throughout the vacuum chamber, so their partial pressures increase up to new steady-state values. (2) At approximately $t = 20$ s the flag is removed from the path of the NO + CO beam in order to allow for its direct impingement on the
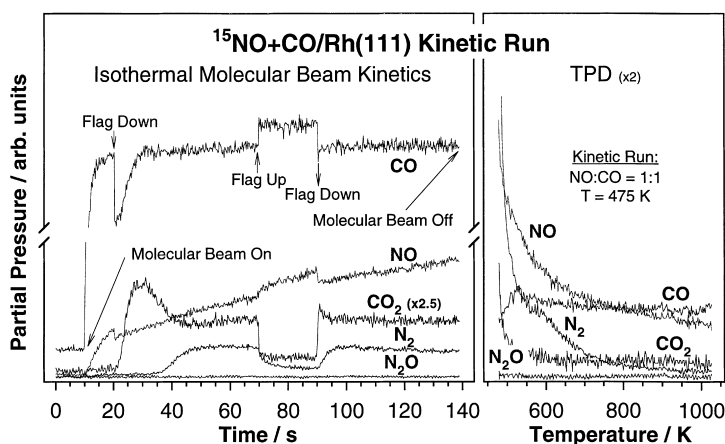

Fig. 1. Left: raw data from a typical isothermal kinetic run of the type described in this report. Right: TPD spectra recorded after the isothermal kinetic run. The heating rate used in the TPD was 10 K/s. Reaction rates and surface coverages can be calculated from these data as described elsewhere [32,33]. Three regimes are distinguished in these experiments, namely, an initial transient right after the exposure of the clean rhodium surface to the beam, a steady-state catalytic region, and a titration/TPD post-mortem analysis of the surface.

surface. This causes both a decrease in the partial pressures of the reactants and an increase in the signals of the products during the transition from a clean surface to the steady-state. The dips in the CO and NO signals are proportional to their apparent sticking coefficient, and the CO_2 and N_2 pressure increases reflect the rate of their formation. Notice that while a change in the CO_2 signal is seen immediately after unblocking the beam, the signal for the formation of N_2 rises only after a delay of about 20 s from that point. (3) The system is allowed to evolve until a steady-state is reached, which in general happens within 50 s after the unblocking of the beam. Neither the adsorption of the reactants nor the desorption of the products change with time under this steady-state condition. (4) During the steady-state regime, the molecular beam is blocked and unblocked deliberately by raising and lowering the flag (at times $t = 70$ and 90 s in this example, respectively) to check the reaction rate values. The clear increases in the partial pressure of the reactants and the accompanying drops in the partial pressure of the products are proportional to the steady-state reaction rates. (5) At about $t = 140$ s, the molecular beam is turned off. After the partial pressures of reactants return to their background levels, the crystal temperature is lowered below 250 K, and the surface is saturated with CO if titration of the O atoms left on the surface is to be performed. (6) Finally, the crystal temperature is ramped at a constant rate of 10 K/s to record the TPD traces for CO and NO (to measure the amount of any unreacted molecules), CO_2 (from CO + O recombination), N_2 and O_2. The CO_2 (from the titration experiments) and N_2 TPD traces allow for the calculation of the coverages of O and N atoms that remain on the surface after stopping the steady-state reaction. A more detailed discussion of this methodology has been published elsewhere [15,16,32,33].

3. Results and discussion

Three regimes can be identified in the kinetic runs described above: (1) a transient behavior within the first 50 s or so after the initial removal of the flag from the path of the beam; (2) the steady-state regime that follows, where the NO + CO conversion is catalytic and (3) the subsequent TPD or CO-titration experiments used to determine the concentration of the

different surface species during the reaction. Separate and complementary mechanistic information can be extracted from each regime.

The first thing that becomes clear from inspection of the raw kinetic data is the fact that the production of molecular nitrogen is rate limiting for the overall NO reduction process. In particular, it is often seen in these experiments that while the rate of CO_2 formation responds immediately to changes (blocking and unblocking) in the beam flux, the nitrogen desorption traces do not. This can in fact be clearly observed in Fig. 1 at $t = 70$ and 90 s. Nitrogen desorption rates and half-life times can be estimated from the temporal evolution of the N_2 mass spectrometer signal right after the beam is intercepted ($t_{1/2} \sim 3$ s in this case) [16].

Systematic measurements were carried out for the steady-state reaction rates as a function of surface temperature, NO + CO beam composition, and total beam flux [15]. A summary of the resulting rates is provided in Fig. 2. Maxima in reaction rates are observed somewhere between 450 and 900 K, the exact temperature
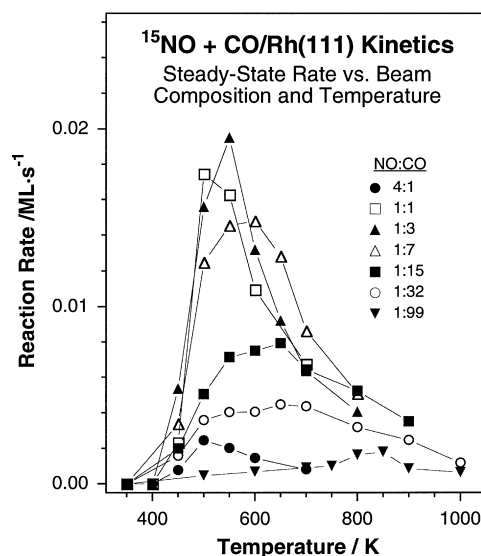

Fig. 2. Overall reaction rate for the $^{15}NO + CO/Rh(1 1 1)$ reaction as a function of temperature and $^{15}NO:CO$ beam ratio. The total flux of the beam was kept constant in all these experiments at $F_{Total} = 0.50$ ML/s. A synergistic effect on reaction rates is seen between the beam composition and the reaction temperature, and reaction rate maxima are reached for beam compositions near stoichiometric and for reaction temperatures between 500 and 600 K.

depending on the NO:CO beam ratio, because a synergistic behavior is seen between increasing CO concentrations in the beam and higher surface temperatures. This behavior can be directly connected with changes in the relative surface coverages for CO and NO on the surface during reaction. A number of pieces of evidence point to the fact that an optimum rate is reached when those coverages follow the 1:1 ratio expected from stoichiometric arguments, as discussed below. The highest absolute reaction rate, which reaches a value close to 0.02 ML/s, was obtained at 550 K and with a 1:3 NO:CO beam composition. This represents a reaction probability of almost 10%, given that the total beam flux in this experiments was set at $F_{\text{Total}} = 0.50$ ML/s.

Initial sticking coefficients were determined for both NO and CO in NO + CO mixtures as a function of surface temperature and beam composition [16]. The changes in s_{NO}^0 with temperature in particular are quite interesting, as they differ from those on clean Rh(1 1 1) [19]. Specifically, the sticking probability for NO changes with both NO:CO ratio and temperature (Fig. 3, left). This indicates that competition with CO alters the kinetics of NO adsorption.

In general, the value of s_{NO}^0 in NO + CO mixtures is lower than that measured for pure NO (about 0.7), but becomes comparable for close to stoichiometric (NO:CO = 1:3 to 1:7) mixtures and moderate (500–700 K) temperatures. Similar arguments can be made for CO, for which the initial sticking coefficient is seen to decrease significantly above about 500 K (Fig. 3, right). Since CO sticking is less probable than NO adsorption in all cases, more CO in the gas phase is required to compensate for this, so that a stoichiometric surface composition can be reached.

In addition to the differences in sticking coefficients, differences in adsorption energies between NO and CO on Rh(1 1 1) are also of great significance to the establishment of the appropriate steady-state surface coverages of the reactants, and as a consequence, to the steady-state reaction rates. Again, the adsorption of NO is clearly stronger than that of CO, as evidenced by the fact that CO is displaced by NO [16]. From both the dependence of the steady-state rates on coverage and temperature (Fig. 2) and the transient behavior of this system (see below), the energy of adsorption of NO was estimated to be approximately 11.5 ± 1.0 kcal/mol higher than that of CO. This is the reason why the rate
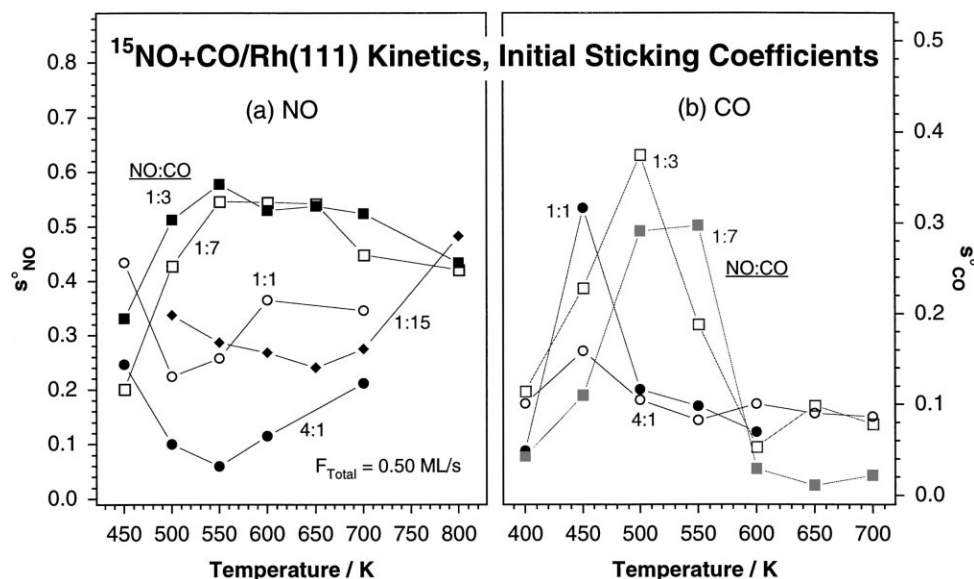

Fig. 3. Initial sticking coefficients for the adsorption of NO (s_{NO}^0, left) and CO (s_{CO}^0, right) from NO:CO beams on Rh(1 1 1) surfaces as a function of surface temperature and beam composition. The total flux was kept constant in all these experiments at $F_{\text{Total}} = 0.50$ ML/s. In general, s_{NO}^0 goes through a maximum at the conditions required for optimum surface stoichiometric NO and CO coverages, while s_{CO}^0 often starts to decrease at lower temperatures than s_{NO}^0.

of NO + CO conversion is optimum with somewhat CO-rich beams.

A number of systematic variations in the transient correlate well with the overall steady-state reaction rates [16]. Specifically, there is a time delay in the production of molecular nitrogen because of the need to build up a threshold atomic nitrogen coverage on the surface before the start of the reaction. The coverage of this nitrogen, as calculated by the time delay in the transient state, corresponds to that observed by TPD afterwards (see below). That coverage increases at a given temperature as the beam becomes richer in CO. Coverage differential parameters ($\Delta\Theta^{\mathrm{Trans}}$), as defined by the coverages of the surface species (nitrogen and oxygen atoms) deposited during the initial stages of the reaction minus those expected if steady-state were to be reached immediately after the start of the reaction, were found to correspond with the behavior of the steady-state rates as a function of temperature and beam composition. The data for the case of nitrogen are shown in Fig. 4. These data were used to estimate the adsorption energy difference between CO and NO reported above.

The relation between the steady-state NO + CO conversion rates and the nitrogen coverages proved to be reasonably complex [32]. This is so at least in part because two types of kinetically-different nitrogen atoms were identified on the surface (Fig. 5). On the one hand, the deposition of a critical coverage of strongly-bonded nitrogen is required for the start of the N_2 desorption step, as mentioned above. This threshold coverage is quite large at low temperatures, amounting to over half a monolayer around 400 K, but decreases abruptly above 600 K, and is fairly insensitive to the ratio of NO to CO in the reaction mixture. On the other hand, an additional small amount of nitrogen appears to be present on the surface during catalysis but to desorb rapidly after the removal of the gas-phase reactants (the blocking of the beam). The NO reduction rate displays an approximately first-order dependence on the coverage of these latter labile N atoms.

Isotope switching experiments indicated that the two kinetically-different nitrogen species are not likely to represent different adsorption sites, but rather similar adsorption states with adsorption energetics modified by their immediate surrounding environment on the surface. The effect of isotopic switching on the surface coverages of the different nitrogen isotopes could be explained by a kinetic model in which the nitrogen atoms form surface islands. Indeed, the time dependence of the removal of one type of surface nitrogen
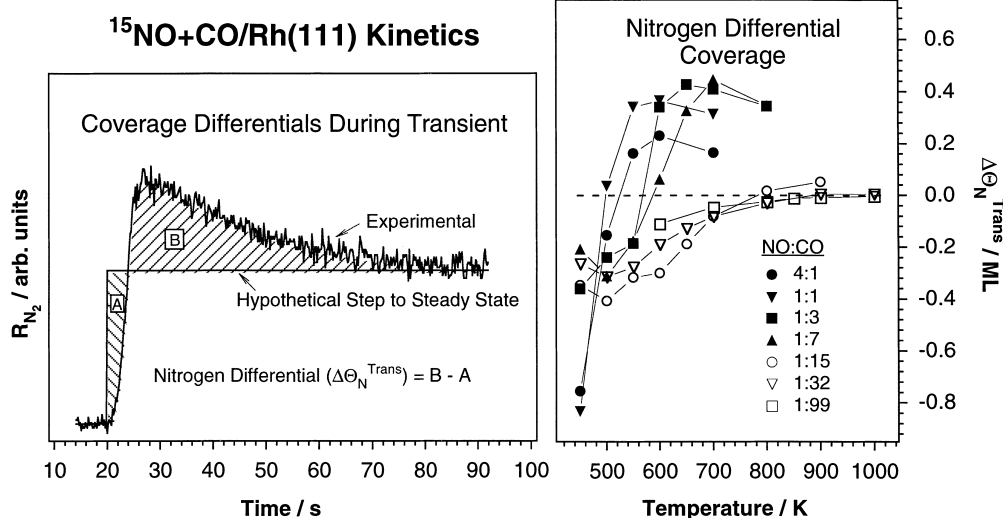

Fig. 4. Left: method used to calculate $\Delta\Theta^{\mathrm{Trans}}$, as given by the shaded areas. Right: transient nitrogen coverage differential as a function of temperature and beam composition. There is a clear demarcation in behavior between NO-rich (4:1 to 1:7) and CO-rich (1:15 to 1:99) beams. Steady-state reaction rates reach a maximum with all beam composition when $\Delta\Theta^{\mathrm{Trans}}$ is close to zero.
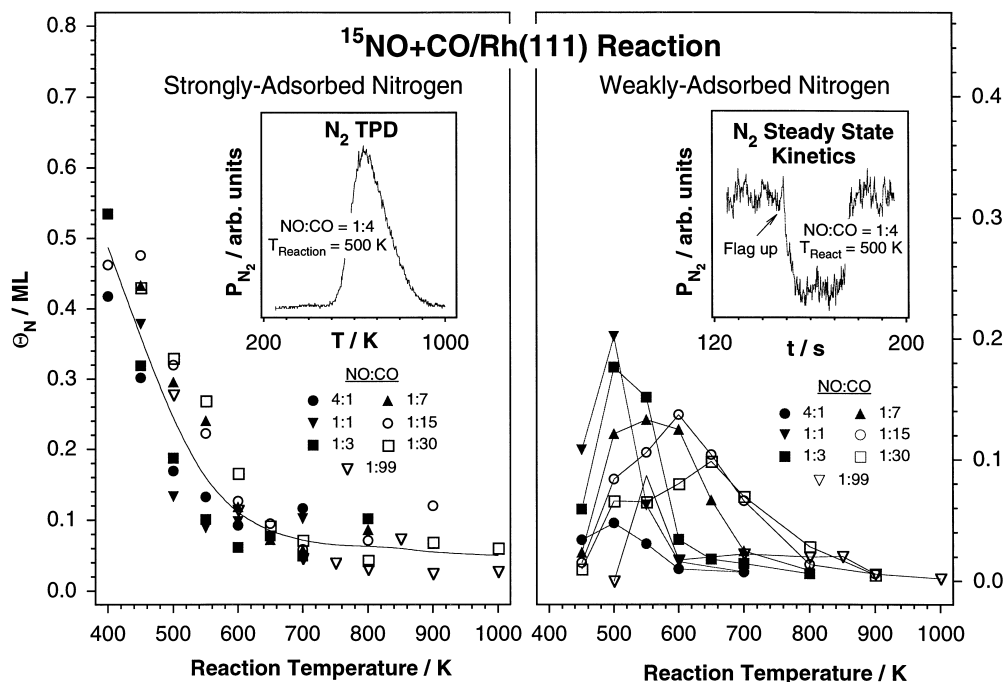
Fig. 5. Nitrogen steady-state coverages as a function of reaction temperature and beam composition. Strongly-bonded nitrogen coverages (left) were calculated from TPD data (left inset), while weakly-bonded nitrogen coverages (right) were estimated from data obtained by blocking the beam during the steady-state portion of the kinetic runs (right inset). Note that the coverage of the strongly-held nitrogen decreases sharply with reaction temperature. The coverage of the weakly-bonded reactive nitrogen is usually low, never exceeding 0.2 ML, and peaks around 500–600 K and close to stoichiometric NO + CO mixtures.

(^{14}N) by the other (^{15}N) was successfully simulated by assuming preferential reactivity from the periphery of such islands together with a small but finite probability for atoms in the core to reach such island edges [32]. Both the data and the corresponding results from our simulation of the time evolution of the coverages of ^{14}N and ^{15}N on the surface are shown in Fig. 6.

Finally, in addition to the studies on the time evolution of the surface coverages of the different types of nitrogen, mechanistic information was also extracted from our measurements of steady-state nitrogen formation rates as a function of the time delay after isotopic switching [34,35]. One of the most important results from such studies is that, upon switching ^{14}NO to ^{15}NO (which could be done in a period of time as short as 3–4 s), no ^{14}N^{14}N is ever produced; the removal of ^{14}N from the surface occurs via the exclusive formation of ^{14}N^{15}N. Fig. 6 displays steady-state rates of formation for all three nitrogen

molecule isotopomers as a function of the time Δt the ^{14}N-covered surface is exposed to the ^{15}NO + CO beams. 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. Otherwise (that is, if N$_2$ is produced by recombination of two surface nitrogen atoms [14,15]), significant amounts of ^{14}N^{14}N would be produced right after the isotope switching, because at that point the surface is mostly covered with ^{14}N. The most likely way for the undissociated NO to participate in molecular nitrogen formation is via the formation and subsequent decomposition of an N–NO surface intermediate.

The mechanistic picture that emerges from these studies can be summarized as follows (Fig. 7). First, a threshold coverage of atomic nitrogen builds up in the form of surface islands during the transient from clean rhodium to the steady-state regime. Since the
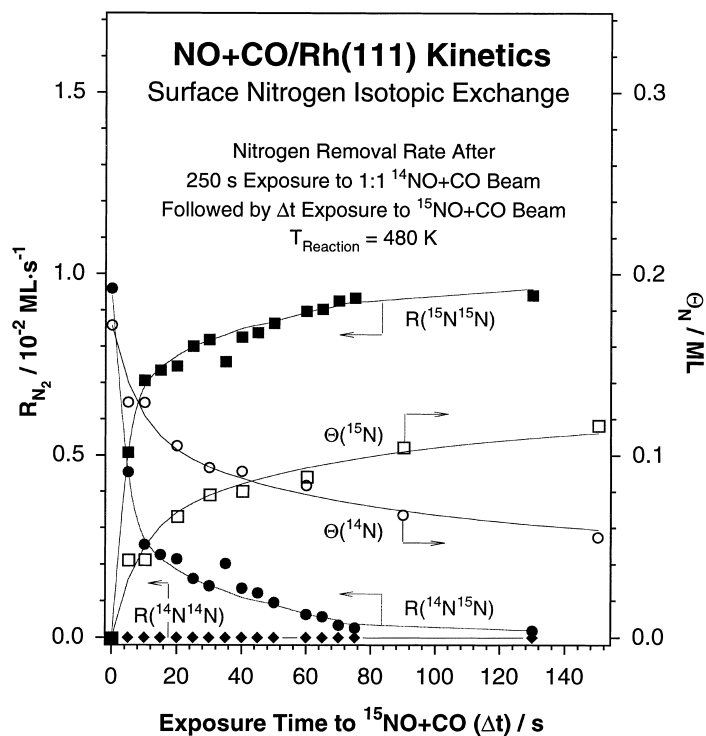
Fig. 6. Evolution of the $^{14}N^{14}N$, $^{14}N^{15}N$ and $^{15}N^{15}N$ production rates (filled symbols), and of the ^{14}N and ^{15}N surface coverages (hollow symbols), during the steady-state reduction of NO with CO on Rh(1 1 1) as a function of the time Δt the ^{14}N-covered surface is exposed to $^{15}NO + CO$ beams. 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.

reactivity of the surface species is affected by their coverages, those nitrogen islands need to acquire a critical size before the catalytic cycle can be sustained. Once that point is reached, however, new incoming NO molecules can diffuse to the edges of the islands, and form N–NO surface complexes before dissociating into N_2 (g) and O (ads). The atomic oxygen byproduct of this step is quickly removed in the form of CO_2 by the CO in the gas mixture, and the nitrogen vacancy generated is replenished via the dissociation of a new NO molecule followed by another CO + O recombination step. The overall catalytic cycle can then be repeated indefinitely.

Our conclusion has significant implications for the mechanism of catalytic NO reduction processes. In particular, 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 NO surface concentration. It is important to point out that the N + N → N_2 reaction is in fact quite feasible on Rh(1 1 1) [29,35], and that at low-temperatures ($T < 500$ K) N_2 formation from NO does not appear to involve a direct N–NO interaction. Our results only indicate that atomic nitrogen recombination is not the dominant step in nitrogen production during the catalytic reduction on NO [15,32]. 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 [36]. Since this is what would be expected if the formation of both products involves a common intermediate, the high pressure work validates our mechanism, and suggests that it may remain applicable under more realistic conditions.

Kinetic Model for the Catalytic Reduction of NO by CO on Rhodium Surfaces
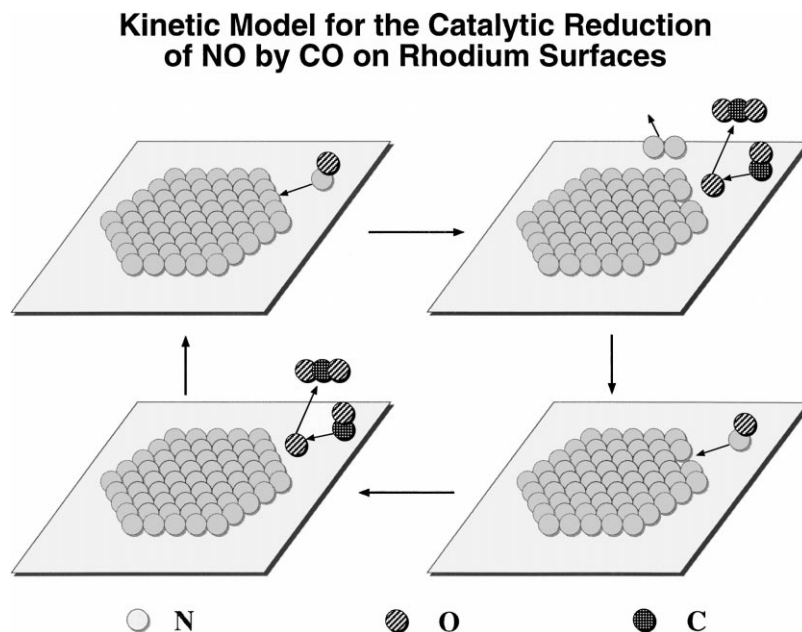

Fig. 7. Schematic depiction of the kinetic model proposed to explain the results obtained in this study. The two key features of this model are: (1) the formation of nitrogen islands and (2) the preferential reaction of the edge N atoms with incoming NO molecules to form N_2 via a N–NO surface intermediate.

4. Conclusions

A summary of our molecular beam work on the catalytic reduction of NO by CO on Rh(1 1 1) single crystal surfaces has been provided. Some interesting conclusions were reached. First, it was found that, since NO adsorbs more strongly on the surface than CO, CO-rich gas mixtures are required to optimize the rate of reaction. It was also determined that the effect of changing gas composition can be partially compensated by changes in reaction temperature, although this cannot be taken to extremes because other pathways (CO poisoning, O deposition) may become operative. Second, it was concluded that, under steady-state conditions, the surface of the metal catalyst is mainly covered with atomic nitrogen. Even though most of this nitrogen is strongly adsorbed on the metal, its energy of adsorption is modified by the local surface arrangement of atoms in such a way so its reactivity is increased. We propose that this happens via the formation of adsorbate islands, the periphery of which react with incoming NO molecules to produce molecular nitrogen. Finally, isotopic labeling experiments strongly suggest that the N_2 production rate-limiting step occurs via the formation of a N–NO surface intermediate. Accordingly, the selectivity of a given catalyst towards nitrogen formation may depend mostly on its ability to preferential break the N–O bond of that N_2O intermediate before it desorbs. Although, these experiments have been carried out on a model surface and under vacuum conditions, the resulting steady-state catalytic behavior is likely to reflect that seen under more realistic conditions.

Acknowledgements

References

[1] K.C. Taylor, Catal. Rev. Sci. Eng. 35 (1993) 457.
[2] M. Shelef, G.W. Graham, Catal. Rev. Sci. Eng. 36 (1994) 433.
[3] V.P. Zhdanov, B. Kasemo, Surf. Sci. Rep. 29 (1997) 31.

[4] T.W. Root, G.B. Fisher, L.D. Schmidt, J. Chem. Phys. 85 (1986) 4687.

[5] S.B. Schwartz, G.B. Fisher, L.D. Schmidt, J. Phys. Chem. 92 (1988) 389.

[6] C.H.F. Peden, D.N. Belton, S.J. Schmieg, J. Catal. 155 (1995) 204.

[7] D.N. Belton, S.J. Schmieg, J. Catal. 144 (1993) 9.

[8] L.H. Dubois, P.K. Hansma, G.A. Somorjai, J. Catal. 65 (1980) 318.

[9] W.C. Becker, A.T. Bell, J. Catal. 84 (1983) 200.

[10] R.E. Hendershot, R.S. Hansen, J. Catal. 98 (1986) 150.

[11] B.K. Cho, J. Catal. 148 (1994) 697.

[12] K.Y.S. Ng, D.N. Belton, S.J. Schmieg, G.B. Fisher, J. Catal. 146 (1994) 394.

[13] S.H. Oh, J. Catal. 124 (1990) 477.

[14] H. Permana, K.Y.S. Ng, C.H.F. Peden, S.J. Schmieg, D.K. Lambert, D.N. Belton, J. Catal. 164 (1996) 194.

[15] C.S. Gopinath, F. Zaera, J. Catal. 186 (1999) 387.

[16] C.S. Gopinath, F. Zaera, J. Phys. Chem. B 104 (2000) 3194.

[17] T.W. Root, L.D. Schmidt, G.B. Fisher, Surf. Sci. 134 (1983) 30.

[18] T.W. Root, L.D. Schmidt, G.B. Fisher, Surf. Sci. 150 (1985) 173.

[19] M. Aryafar, F. Zaera, J. Catal. 175 (1998) 316.

[20] C.H.F. Peden, D.W. Goodman, D.S. Blair, P.J. Berlowitz, G.B. Fisher, S.H. Oh, J. Phys. Chem. 92 (1988) 1563.

[21] B.K. Cho, B.H. Shanks, J.E. Bailey, J. Catal. 115 (1989) 486.

[22] S.H. Oh, G.B. Fisher, J.E. Carpenter, D.W. Goodman, J. Catal. 100 (1986) 360.

[23] S.H. Oh, J.E. Carpenter, J. Catal. 101 (1986) 114.

[24] L.A. DeLouise, N. Winograd, Surf. Sci. 159 (1985) 199.

[25] H.J. Borg, J.F.C.-J.M. Reijerse, R.A. van Santen, J.W. Niemantsverdriet, J. Chem. Phys. 101 (1994) 10052.

[26] T.W. Root, G.B. Fisher, L.D. Schmidt, J. Chem. Phys. 85 (1986) 4679.

[27] C.-T. Kao, G.S. Blackman, M.A. Van Hove, G.A. Somorjai, C.-M. Chan, Surf. Sci. 224 (1989) 77.

[28] D.N. Belton, C.L. DiMaggio, S.J. Schmieg, K.Y.S. Ng, J. Catal. 157 (1995) 559.

[29] D.N. Belton, C.L. DiMaggio, K.Y.S. Ng, J. Catal. 144 (1993) 273.

[30] J. Liu, M. Xu, T. Nordmeyer, F. Zaera, J. Phys. Chem. 99 (1995) 6167.

[31] H. Öfner, F. Zaera, J. Phys. Chem. 101 (1997) 396.

[32] F. Zaera, C.S. Gopinath, J. Chem. Phys. 111 (1999) 8088.

[33] F. Zaera, J. Liu, M. Xu, J. Chem. Phys. 106 (1997) 4204.

[34] F. Zaera, C.S. Gopinath, Chem. Phys. Lett., 2000, in press.

[35] F. Zaera, C.S. Gopinath, 2000, in preparation.

[36] H. Permana, K.Y.S. Ng, C.H.F. Peden, S.J. Schmieg, D.N. Belton, J. Phys. Chem. 99 (1995) 16344.