

Available online at www.sciencedirect.com



Chemical Physics Letters 388 (2004) 201-207

CHEMICAL PHYSICS LETTERS

www.elsevier.com/locate/cplett

Nitrogen removal pathways in a steady-state NO + CO reaction on Pd(110)

Yunsheng Ma^a, Izabela Rzeznicka^b, Tatsuo Matsushima^{a,*}

^a Catalysis Research Center, Hokkaido University, Sapporo 001-0021, Japan ^b Graduate School of Environmental Earth Science, Hokkaido University, Sapporo 060-0810, Japan

> Received 20 January 2004; in final form 23 February 2004 Published online: 20 March 2004

Abstract

Three removal processes of surface nitrogen, i.e., (i) the decomposition of the intermediate $N_2O(a)$, (ii) its desorption without decomposition and (iii) the associative desorption of nitrogen atoms, were separately studied in a steady-state NO + CO reaction on Pd(110) through analysis of the angular and velocity distributions of desorbing products N_2 and N_2O . At temperatures below approximately 600 K, the processes (i) and (ii) prevailed, whereas at higher temperatures, the process (iii) contributed significantly. The branching was also sensitive to the CO/NO pressure ratio. © 2004 Elsevier B.V. All rights reserved.

1. Introduction

The decomposition of NO over metal catalysts such as palladium and rhodium yields N₂O, which has a remarkable greenhouse effect, concomitantly with N₂ [1]. Reducing of N₂O is highly desired on improved catalysts. This Letter delivers the first analysis of three surface nitrogen-removal processes, i.e., (i) the decomposition of the intermediate, $NO(a) + N(a) \rightarrow$ $N_2O(a) \rightarrow N_2(g) + O(a)$, (ii) N_2O desorption without decomposition and (iii) the associative desorption of nitrogen atoms, $2N(a) \rightarrow N_2(g)$, in a steady-state NO + CO reaction on Pd(110). This separation is possible in angle-resolved product desorption analysis (AR-PDA) combined with cross-correlation time-of-flight (TOF) techniques since the $N_2O(a)$ decomposition emits N₂ in an inclined way, whereas the associative desorption of N(a) collimates along the surface normal [2–4]. The branching changed with the surface temperature and the NO/CO pressure ratio.

Ordinary kinetic measurements at the steady-state NO+CO reaction are not informative for surface nitrogen-removal processes because the overall rate is controlled by NO dissociation [5]. On the other hand, the angular and velocity distributions of desorbing products can provide information of the final desorption process whenever any step becomes ratedetermining since these distributions do not directly involve the reaction rate and are always related to the product desorption [6]. These distributions were frequently analyzed in the course of catalyzed NO decomposition with several transient methods to avoid the well-known large N₂ formation on the reaction chamber wall, such as modulated-molecular beams (MMB) [7,8] and AR-temperature programmed desorption (TPD) [2,9–11]. Steady-state conditions, however, cannot be established for the reaction because of the periodical change of reactants in MBS. Similar ambiguities were also induced in AR-TPD in the presence of gaseous reactants. Neither angular nor velocity distributions have been reported under steadystate NO+CO reactions except for our earlier work [12,13]. In the present work, AR-PDA was successfully performed for the steady-state NO+CO reaction over a wide range of reactant pressures by using a gas doser with a fine orifice.

^{*}Corresponding author. Fax: +81-011-706-9120.

E-mail address: tatmatsu@cat.hokudai.ac.jp (T. Matsushima).

^{0009-2614/\$ -} see front matter \odot 2004 Elsevier B.V. All rights reserved. doi:10.1016/j.cplett.2004.02.090

2. Experiments

The apparatus, which had three chambers separately pumped, was described previously [14,15]. The reaction chamber has reverse-view low-energy electron diffraction and X-ray photoelectron spectroscopy optics, an ion gun, and a quadrupole mass spectrometer (QMS) for angle-integrated (AI) measurements and monitoring the partial pressures of reactants (P_{NO} and P_{CO}). The chopper house, which had a pumping rate of about 7 m³ s⁻¹ for a high angle-resolution [16], has a narrow slit facing the reaction chamber and a cross-correlation random chopper blade. The analyzer, connected through a narrow tube, is equipped with another QMS for AR-PDA and TOF analyses. The distance from the ionizer to the chopper blade was 377 mm and the time resolution was selected at 20 µs.

A gas mixture of ¹⁵NO and ¹³CO was introduced through a doser with a small orifice (diameter; 0.1 mm) about 2 cm from a sample crystal. For pressure-dependence measurements, ordinary CO was additionally backfilled. The products ¹⁵N₂, ¹³CO₂ and ¹⁵N₂O signals were monitored in both AI and AR forms. Hereafter, these are described as N₂, CO₂ and N₂O in the text. The desorption angle (polar angle; θ) was scanned in the plane along the [0 0 1] direction. The fragmentation of N₂O in both QMS was corrected.

3. Results

3.1. General features

The AR signal was obtained by the analyzer QMS as the difference (ΔN_2 for the N_2 signal, for example) between the signal at the desired angle and the signal when the crystal was away from the line-of-sight position. The AR signals at $\theta = 0^{\circ}$ for desorbing N₂, CO₂ and N₂O, and the AR N₂ signal at $\theta = 41^{\circ}$ are displayed because of their collimation angles as a function of the surface temperature (T_S) in Fig. 1a. All the signals in the steadystate NO + CO reaction were negligible below 480 K. The N_2 signal at $\theta = 41^\circ$ increased rapidly above 500 K with increasing $T_{\rm S}$ to a maximum at around 550 K and then decreased at higher temperatures. The N₂ signal at $\theta = 0^{\circ}$, on the other hand, increased slowly and peaked at about 600 K. These differences in AR-N₂ signals imply a branching shift of N_2 formation pathways with T_S . No hysteresis was found in their signals with decreasing $T_{\rm S}$.

The above small orifice was effective to reduce N_2 formation on the chamber wall, improving the AI-signal. Under this construction, the flux of incident reactants towards the surface decreased proportionally to $\cos(\theta)$ when the angle shifted from the normal direction. This decrement was evaluated by monitoring the AR-signal of N₂O, which should follow the cosine distri-



Fig. 1. (a) $T_{\rm S}$ -dependence of AR-signals of products with a (${}^{15}\rm NO:{}^{13}\rm CO=1:4$) mixture at 2.5×10^{-5} Torr. (b) ${}^{15}\rm NO$ incidence pressure dependence of the AR- ${}^{15}\rm N_2$ and ${}^{15}\rm N_2O$ signals at $\theta = 0^{\circ}$ at fixed CO, and of the ${}^{15}\rm N_2$ signals at $\theta = 41^{\circ}$. The ${}^{15}\rm N_2O$ fragmentation was corrected for the ${}^{15}\rm N_2$ signals.

bution because of the Maxwellian velocity curves at the surface temperature all over the angle [17]. The signal intensity was corrected by this effect.

3.2. Angular distribution

The CO₂ desorption sharply collimated along the surface normal in a $\cos^{13-16}(\theta)$ form. On the other hand, N₂ desorption showed an inclined form collimated at around 40° off the surface normal below about 600 K. At higher temperatures, both the normally directed and cosine components were enhanced. The N₂ signal at 40° increased rapidly with P_{NO} (Fig. 1b), whereas it showed a critical CO pressure in its P_{CO}-dependence (Fig. 2a). Thus, each desorption component should be derived from angular and velocity distribution analyses.

The $AR-N_2$ signal is plotted against the desorption angle in Fig. 2b. The total pressure with a mixture



Fig. 2. (a) $P_{\rm CO}$ -dependence of the AR-¹⁵N₂ signals at $\theta = 0^{\circ}$ and 40° at a fixed ¹⁵NO pressure and $T_{\rm S} = 550$ K. (b,c) Angular distributions of desorbing ¹⁵N₂ at different $P_{\rm CO}$.

(NO:CO = 3:1) was fixed at 5.7×10^{-6} Torr and $T_{\rm S} = 550$ K. The N₂ distribution was in an inclined way approximated as $\cos^{28}(\theta - 40)$. The signals at 40° and 0° are plotted against $P_{\rm CO}$ in logarithm scales, where only ¹⁵NO was dosed through the orifice, and ¹²CO was backfilled (Fig. 2a). With increasing P_{CO} , the signal at 40° increased steeply with a slope of 1.8 and reached a steady level above the ratio of $P_{\rm CO}/P_{\rm NO} = 0.7$. The ratio of the signal at 0° to that at 40° was kept under 0.05 over a wide CO pressure range. On the other hand, at 640 K, the signal ratio increased to about 0.7 with increasing $P_{\rm CO}$ up to $P_{\rm CO}/P_{\rm NO} = 4$, where it showed a constant value (Fig. 3a). Below this ratio, the angular distribution changed, i.e., at low P_{CO} , the N₂ desorption was fairly in the inclined way (Fig. 3b). At high P_{CO} , the signal at $\theta = 0^{\circ}$ was enhanced, i. e., the desorption including the normally directed and cosine components became dominant (Fig. 3c and d).

3.3. Velocity distribution

The translational temperature of desorbing CO₂ was about 3 times higher than the surface temperature at $\theta = 0^{\circ}$ and decreased quickly with increasing θ , being consistent with the normally directed desorption. The translational temperature of N₂ was very high, more than twice that of CO₂. Typical velocity curves of N₂ at 550 K are shown in Fig. 4. The apparent translational temperature calculated from the average kinetic energy $(\langle E \rangle)$ as $T_{\langle E \rangle} = \langle E \rangle / 2k$ is shown in $\langle \rangle$ in the figure, where *k* is the Boltzmann constant. The value was maximized to 3700 K at $T_S = 550$ K at around the collimation angle and to a similar value at $T_S = 640$ K (Fig. 5). It decreased quickly with an increasing shift from the collimation angle, consistently with the inclined desorption.

The velocity distributions of desorbing N₂ at $\theta = 0^{\circ}$ commonly showed a significant thermalized component to the surface temperature. Its intensity should be equal to the cosine component involved in the angular distributions in Figs. 2 and 3. In velocity curve analysis, its contribution was first subtracted from the observed curves. The resultant distributions were still broad, yielding the speed ratio (SR) defined as $(\langle v^2 \rangle / \langle v \rangle^2 -1)^{1/2}/(32/9\pi - 1)^{1/2}$ of 1.1 at 640 K even at the collimation position. Here, v is the velocity of N₂, $\langle v \rangle$ is the mean velocity, and $\langle v^2 \rangle$ is the mean square velocity. This suggests that the resultant velocity curve still involves two or more components. To deconvolute into two fast



Fig. 3. (a) P_{CO} -dependence of the AR-¹⁵N₂ signals at $\theta = 0^{\circ}$ and 40° at fixed ¹⁵NO. (b–d) Angular distributions of desorbing ¹⁵N₂ at different P_{CO} . The intensity was normalized to the maximum in (d). Typical deconvolutions are drawn by broken curves.

components, the modified Maxwellian distribution, $f(v) = v^3 \exp\{-(v - v_0)^2/\alpha^2\}$, was fitted to each component, where f(v) is the modified Maxwellian distribution function, v_0 is the stream velocity and α is the width parameter.

It is difficult to determine each modified Maxwellian uniquely because each form involves two parameters. In the present study, only three parameters were determined by curve fittings at high- and low-velocity sides. To omit the fourth parameter, we simply assumed a common width parameter. In this treatment, the energy of the faster component would be somewhat underestimated, and that of the other should be overestimated because the faster component is likely to yield a smaller α value. The resultant deconvolutions are shown by broken curves in Figs. 4 and 5. The fastest component yielded a translational temperature of 5500-6400 K at $\theta = 40-50^{\circ}$ and an SR of 0.7. The second component showed values of around 2000–3000 K and SR = 0.94. There are significant differences in the velocity curves from the previous work [12,13]. The observation of high-velocity signals in the range of 2.5–4 km s⁻¹ might be obscured in the high background in the previous work because of low reactant pressures.

4. Discussion

4.1. Desorption components

The above three pathways (i), (ii) and (iii) are operative. The quantity of $[CO_2]/\{[N_2] + [N_2O]\}$ was kept at unity over the conditions studied, confirming no other paths removing surface nitrogen or oxygen. $[CO_2], [N_2]$ and $[N_2O]$ designate the amount of produced CO_2 , N_2 and N_2O estimated from the AI-signals. According to these cooperative pathways, the product ratio must be $[CO_2]:[N_2]:[N_2O] = 2x + y:x:y$, where x and y represent the progress of N₂ formation in the processes (i) and (iii), and that of N₂O in the process (ii). The x/y ratio represents the branching of N_2/N_2O formation. The observed ratio steeply increased with increasing temperature or CO pressure.

The total amount of desorbed species can also be estimated from the AR-signal at the collimation angle, the sharpness of the angular distribution and the mass sensitivity correction due to velocity [18]. The observed signal at the collimation angle is proportional to the reaction rate under the condition that the angular and velocity distributions remain invariant. In other words,



Fig. 4. Velocity distributions of ${}^{15}N_2$ at $T_S = 550$ K, at $\theta = 0^{\circ}$ and 41° , and at different ${}^{15}NO/{}^{13}CO$ ratios at a fixed ${}^{15}NO$ pressure of 5×10^{-6} Torr. The average kinetic energy is indicated in $\langle \rangle$. Typical deconvolutions are drawn by broken curves. The solid line indicates their summation.

the kinetics must be separately treated for each component with different distributions. The observed angular distribution was approximated as $0.92\{\cos^{28}(\theta + 41) + \cos^{28}(-41)\} + 0.06\cos^{5}(\theta) + 0.08\cos(\theta)$ at $T_{\rm S} = 550$ K with the ratio of NO:CO = 1:4 (Fig. 2c). The pre-factors indicate the relative intensity. At 640 K, the distribution became $0.57\{\cos^{28}(\theta + 41) + \cos^{28}(\theta - 41)\} +$ $0.28\cos^{5}(\theta) + 0.47\cos(\theta)$ (Fig. 3d), where the desorbed amount in the inclined way was about 25% of the total N₂ formation [18]. At higher temperatures, the inclined desorption was mostly suppressed, yielding a shift in the reaction pathways.

4.2. Kinetics of each process

Around the optimum temperature or below it, the surface nitrogen is removed either through the inclined desorption in (i) or as N₂O in (ii). The former shares about 80% with a mixture (NO:CO = 1:1). Both processes need the preceding process of N(a) + NO(a) \rightarrow N₂O(a), which may be enhanced with increasing either

 $P_{\rm NO}$ or $P_{\rm CO}$ because of increasing NO(a) or vacant sites. The latter is created by removal of O(a). In fact, N_2 inclined desorption showed near 2nd order in CO below the critical P_{CO} value (Fig. 2a). At high P_{CO} , the surface oxygen is mostly removed by CO and then the rate becomes insensitive to $P_{\rm CO}$. On the other hand, at high temperatures, the associative process (iii) fairly removes the surface nitrogen because it has a higher activation energy [2] and the processes (i) and (ii) are suppressed by decreasing amounts of NO(a). At high temperatures above 600 K, the NO(a) density is low at low $P_{\rm NO}$, where the process (iii) prevails (Fig. 3a), but the processes (i) and (ii) are dominated at high P_{NO} (Fig. 1b). In fact, at 640–680 K, the N₂ desorbed at $\theta = 0^{\circ}$ is highly thermalized. The amount of the thermalized component after the distribution corrections reached about 40% of the N_2 total formation at low P_{CO} [18]. With increasing $P_{\rm CO}$, it increased linearly as well as the normally directed fast N₂, whereas the signal at $\theta = 40^{\circ}$ remained invariant or decreased. The thermalized component is likely to be formed via the associative process.



Fig. 5. Velocity distributions of ${}^{15}N_2$ at 640 K, at $\theta = 0^{\circ}$ and 41°, and at different ${}^{15}NO/{}^{13}CO$ ratios at a fixed ${}^{15}NO$ pressure of 5×10^{-6} Torr. The average kinetic energy is indicated in $\langle \rangle$. Typical deconvolutions are drawn by broken curves.

4.3. Comparison with other conditions

The inclined N_2 desorption was first found by Ikai and Tanaka [9], who performed AR-TPD measurements of the product N_2 on Pd(110) in the presence of gaseous NO and H₂ or CO. They proposed 'the desorptionmediated reaction without the intermediate $N_2O(a)$ ' for this off-normal desorption because only the heating procedure yielded the peculiar desorption and not in their subsequent cooling [2,9]. However, this is not surprising because in their heating, the surface was initially covered by NO, whereas in the subsequent cooling, the absence of inclined desorption may be due to insufficient NO(a). In addition, the intermediate N(a)would be mostly removed as NH3 at their conditions of $NO \ll H_2$. In fact, the N₂O formation in the process (i) is highly sensitive to the amount of NO(a) and N(a) as described above.

5. Summary

The analysis of both angular and velocity distributions of desorbing products N_2 and N_2O has separated three surface nitrogen-removal processes involved in a steady-state NO + CO reaction on Pd(110). The pathway through the intermediate N₂O(a) prevails below 600 K and at lower P_{CO} , whereas, at high temperatures and high P_{CO} , the associative desorption of nitrogen atoms dominates the removal.

Acknowledgements

Izabela Rzeznicka is indebted to the Ministry of Education, Science, Sports and Culture of Japan for a 2000–2004 scholarship.

References

- V.I. Pârvulescu, P. Grange, B. Delmon, Catal. Today 46 (1998) 233.
- [2] M. Ikai, K.I. Tanaka, J. Phys. Chem. B 103 (1999) 8277.
- [3] Y. Ohno, K. Kimura, M. Bi, T. Matsushima, J. Chem. Phys. 110 (1999) 8221.
- [4] H. Horino, S. Liu, A. Hiratsuka, Y. Ohno, T. Matsushima, Chem. Phys. Lett. 341 (2001) 419.

- [5] F. Garin, Appl. Catal. A General 222 (2001) 183.
- [6] I. Kobal, I. Rzeznicka, T. Matsushima, Recent Res. Develop. Phys. Chem. Transworld Res. Network 6 (2002) 391.
- [7] J.I. Colonell, K.D. Gibson, S.J. Sibener, J. Chem. Phys. 104 (1996) 6822.
- [8] F. Zaera, C.S. Gopinath, Chem. Phys. Lett. 332 (2000) 209.
- [9] M. Ikai, K.I. Tanaka, Surf. Sci. 357/358 (1996) 781.
- [10] M. Ikai, N.M.H. Janssen, B.E. Nieuwenhuys, K.I. Tanaka, J. Chem. Phys. 106 (1997) 311.
- [11] M. Ikai, K.I. Tanaka, J. Chem. Phys. 110 (1999) 7031.

- [12] I. Kobal, K. Kimura, Y. Ohno, T. Matsushima, Surf. Sci. 445 (2000) 472.
- [13] I. Kobal, K. Kimura, Y. Ohno, H. Horino, I. Rzeźnicka, T. Matsushima, Studies Surf. Sci. Catal. 130 (2000) 1337.
- [14] T. Matsushima, Surf. Sci. Rep. 52 (2003) 1.
- [15] I. Rzeznicka, Md.G. Moula, L. Morales, Y. Ohno, T. Matsushima, J. Chem. Phys. 119 (2003) 9829.
- [16] M. Kobayashi, Y. Tuzi, J. Vac. Sci. Technol. 16 (1979) 685.
- [17] T. Matsushima, Catal. Surv. Jpn. 5 (2002) 71.
- [18] G. Cao, Md.G. Moula, Y. Ohno, T. Matsushima, J. Phys. Chem. B 103 (1999) 3235.