C-N Coupling in Reactions between Atomic Nitrogen and Ethylene on Rh(111)

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Reactions between adsorbed atomic nitrogen and ethylene on Rh(111) have been investigated by temperature-programmed reaction spectroscopy (TPRS), secondary ion mass spectrometry (SIMS), and work function measurements. Coadsorption of a small amount of ethylene to 0.10 monolayer of atomic nitrogen results in the formation of a surface cyanide species, which is detected by SIMS through the Rh₂CN⁺ cluster ion. Cyanide formation has been followed by measuring the decrease of the atomic nitrogen and carbon coverages and the accompanied increase in the CN coverage in temperature-programmed SIMS experiments. The CN formation kinetics is described by a preexponential factor and an activation energy of $10^{11\pm1}$ s⁻¹ and 111 ± 10 kJ/mol, respectively. In the absence of surface hydrogen, CN groups are stable up to \sim 700 K. CN decomposition results in reaction-limited desorption of N₂ with a maximum at 800 K and is described by a preexponential factor and an activation energy of $10^{13\pm1}$ s⁻¹ and 210 ± 15 kJ/mol. Coadsorption of large amounts of ethylene to 0.10 monolayer of N_{ads} results in the desorption of almost all nitrogen in the form of HCN between 500 and 700 K. Cyanogen was also observed as a reaction product although the selectivity was small, 3% at maximum. Work function measurements indicate that surface cyanide is present as a negatively charged species on the Rh(111) surface.

Introduction

The reactivity of CN bonds on platinum metals is of interest for large scale industrial processes such as e.g. the Andrussow process for the production of HCN by reaction of CH₄, NH₃, and O₂ over Pt/Rh gauzes at 1050 °C. ¹ Formation of CN bonds has been observed in reduction of NO by hydrocarbons on Rh-supported catalysts, ^{2,3} which is of interest in the context of NO_x reduction from lean burn car exhausts. ^{4,5} HCN synthesis by reaction between CH₄ and NH₃ with selectivities up to 90% has been reported by Hasenberg et al. ⁶ in the moderate pressure regime on Rh foil.

CN surface chemistry shows large variations among the group VIII metals. Whereas CN bond fission proceeds rapidly on the Ni(111) surface,⁷ the Pt(111) surface does not dissociate the surface cyanide bond at all.⁸ Between these two extremes is the reactivity of the surfaces of Pd(111),⁹ Ru(001),¹⁰ and Rh-(111).¹¹

Up to now, most information concerning CN surface chemistry has been gathered from adsorption and decomposition experiments with CN-containing molecules such as C₂N₂,^{11,12} CH₃NH₂,¹² CH₃NO₂,¹³ and H₂NCHO.¹⁴ Literature dealing with the formation of CN on the surface is scarce, however. DeLouise and Winograd¹⁵ reported formation of surface CN upon reaction of NO with carbidic carbon on Rh(331) using secondary ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy (XPS). In a previous temperature-programmed reaction spectroscopy (TPRS)/SIMS investigation on the reactions between NO and ethylene on Rh(111), we observed the production of HCN and the formation of surface cyanides among many other reactions.¹⁶ Although almost all reaction steps could be identified, the situation was too complex to warrant kinetic analysis.

The purpose of this paper is to report on the selectivity of the reaction between atomic nitrogen and ethylene and to present kinetic parameters for the formation of CN by the coupling of atomic nitrogen and atomic carbon on the Rh(111) surface. To reduce the number of surface reactions, we used atomic nitrogen instead of NO as in the previous paper. Temperature-programmed reaction spectroscopy is used to monitor the desorbing products, while temperature-programmed secondary ion mass spectrometry (TPSIMS) monitors reactions on the surface, especially CN formation and decomposition.

Experimental Section

The experiments were done in an ultrahigh vacuum system (base pressure around 10^{-10} mbar) equipped with a Leybold SSM 200 quadrupole mass spectrometer for TPD and (static) SIMS measurements, as described in detail elsewhere. Work function changes were determined by measuring the shift of the low kinetic energy onset of the secondary electron emission in AES. To minimize damage effects due to electron irradiation, we used a primary electron beam of 500 eV and $0.02~\mu$ A. The sample was biased -10.0~V with respect to the ground potential. The onset was defined as the energy at which the derivative of the secondary electron distribution maximizes.

The rhodium crystal, cut in the [111] orientation within 0.5° and polished by standard procedures, was mounted on a moveable stainless steel manipulator with 0.3 mm thick tantalum wires, where it could be cooled to liquid nitrogen temperature and resistively heated to 1500 K. Temperatures were measured with a chromel-alumel thermocouple spotwelded on the backside of the crystal. Small amounts of bulk impurities, such as sulfur, chlorine, and boron, were removed by cycli of argon sputtering (1.5 keV, $5 \mu A/cm^2$) at 900 K and annealing to 1400 K. Carbon was removed by annealing the crystal in 2×10^{-8} mbar O2, by slowly varying the temperature between 900 and 1100 K. Oxygen was removed from the surface by annealing shortly to 1425 K. Ethylene, NO, and H₂ (Messer Griesheim, 99.95%, 99.5%, and 99.999% pure, respectively) were used without further purification; gas exposures are reported in langmuirs (1 langmuir = 1.33×10^{-6} mbar·s); coverages are

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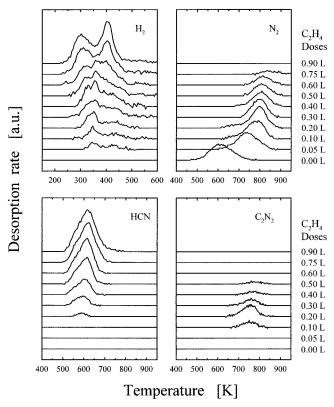


Figure 1. TPRS spectra of H_2 , N_2 , HCN, and C_2N_2 obtained from a Rh(111) surface covered with 0.10 ML of atomic nitrogen and various amounts of ethylene. The ethylene adsorption temperature was 120 K, and the heating rate was 10 K/s.

reported in monolayers (ML, fractional number of adsorbates per Rh surface atom).

Results

Temperature-Programmed Reaction of Atomic Nitrogen and Ethylene. Atomic nitrogen was deposited on the Rh(111) surface by reaction between NO and H_2 . NO was molecularly adsorbed at 120 K, after which it was thermally dissociated by heating to 375 K. Atomic oxygen was selectively removed by exposing the surface to 2×10^{-8} mbar H_2 for 160 s at 375 K. SIMS spectra of the surface after reaction indicated that atomic nitrogen was the only surface species. Assuming a value of 0.68 ML for the NO-saturated surface, 17 calibration toward the NO uptake curve indicated that an atomic nitrogen coverage of 0.10 ML was obtained starting from an NO exposure of 0.25 langmuir. The procedure has been described in detail in a previous publication on the hydrogenation of atomic nitrogen. 18

Figure 1 shows the TPRS spectra of H_2 (2 amu), HCN (27 amu), N_2 (28 amu), and C_2N_2 (52 amu) obtained from a Rh-(111) surface covered with 0.10 ML of N_{ads} and various amounts of ethylene coadsorbed at 120 K. We also monitored CH_3CN (51 amu) and NH_3 (17 amu), but these products were not detected. For comparison, we have added the N_2 desorption spectrum obtained from a surface solely covered with 0.10 ML of atomic nitrogen. Figure 1 shows that, if atomic nitrogen is the only adsorbate, N_2 desorption is completed at 750 K, which is in good agreement with the literature.¹⁹

For the lowest C_2H_4 exposure, 0.05 langmuir, the only observed desorption products are N_2 and H_2 . However, the N_2 desorption maximum has significantly shifted to higher temperatures (from 610 to 730 K). At this ethylene exposure, there is not sufficient atomic carbon (about 0.05 ML) to tie up all the atomic nitrogen as CN. Therefore, the N_2 desorption state

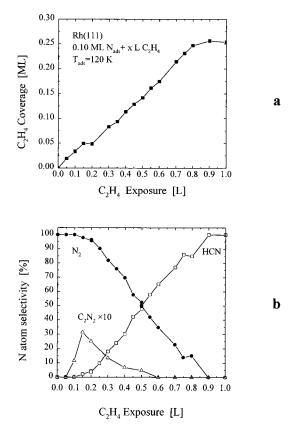


Figure 2. (a) Uptake curve for irreversibly adsorbed C_2H_4 , determined by adding the H_2 and HCN TPD peak areas and assuming a C_2H_4 saturation coverage of 0.25 ML. (b) Distribution of atomic nitrogen over the desorption products N_2 , C_2N_2 , and HCN for various amounts of coadsorbed ethylene.

contains contributions from the N-N recombination limited reaction (at the low-temperature side) and from the CN decomposition limited reaction (at the high-temperature side). With increasing ethylene exposure, all atomic N reacts to CN, the N₂ desorption maximum shifts to 800 K, and the amount of N_{ads} desorbing as N_2 decreases. The latter decrease in N_2 desorption runs parallel with an increase of the HCN desorption, which is observed in a broad state around 600 K, for ethylene exposures above 0.20 langmuir. Small traces of cyanogen (C₂N₂) desorb at 750 K for intermediate ethylene exposures. The H₂ desorption behavior is quite similar to that observed for C₂H₄ decomposition on the clean Rh(111) surface,²⁰ with the exception that no H₂ desorption is observed above 500 K. In the absence of nitrogen, significant desorption of H₂ occurs up to ~ 700 K for high coverages of ethylene on Rh(111).²⁰ The H₂ desorption state with a peak maximum at 400 K is associated with ethylidyne decomposition.

Figure 2a shows the uptake curve for irreversibly adsorbed ethylene, which was constructed by adding up the H_2 and HCN TPD areas and assuming a saturation coverage of 0.25 ML, in conformity with the situation on the empty surface.²⁰ Up to exposures of 0.80 langmuirs, the amount of irreversibly adsorbed C_2H_4 increases linearly with C_2H_4 exposure. This indicates a constant sticking coefficient for C_2H_4 adsorption at 120 K and a mobile precursor state for adsorption, in accordance with the situation on the clean Rh(111) surface.²⁰ For ethylene exposures above 0.80 langmuir, molecular ethylene desorption is observed and the amount of C_2H_4 that decomposes becomes constant as reflected by the constant value for the sum of the H_2 and HCN desorption areas.

Figure 2b shows the distribution of atomic nitrogen over the reaction products HCN, N_2 , and C_2N_2 as a function of the

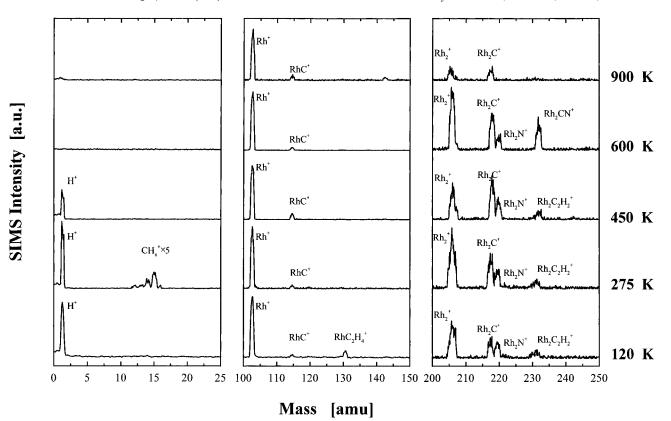


Figure 3. Static SIMS spectra of the Rh(111) surface covered with 0.10 ML of N_{ads} and 0.15 ML of C_2H_4 after heating to the indicated temperature and cooling back to 200 K. Atomic nitrogen is observed by the Rh_2N^+ cluster ion (220 amu) and molecular ethylene by the $Rh_2H_4^+$ cluster ion (131 amu) and several fragmentation products. Ethylidyne is observed by the CH_3^+ cluster ion (and its fragmentation products), and surface CN is detected exclusively by the Rh_2CN^+ cluster ion.

ethylene exposure. Up to ethylene exposures of 0.20 langmuirs, the vast majority of the atomic nitrogen desorbs as N_2 while also small amounts of C_2N_2 are observed. The selectivity toward C_2N_2 maximizes at an C_2H_4 exposure of ≈ 0.15 langmuir, where approximately 3% of the atomic nitrogen leaves the surface as C_2N_2 . For ethylene exposures above 0.20 langmuir, the amount of atomic nitrogen desorbing as HCN increases at the expense of N_2 desorption, and the selectivity to HCN reaches 100% for the highest ethylene exposures.

Static SIMS of Surface Reactions between Atomic Nitrogen and Ethylene. Figure 3 shows three relevant mass regions of SSIMS spectra of the Rh(111) surface, covered with 0.10 ML of N_{ads} and 0.15 ML of ethylene, after heating to the indicated temperatures and cooling to 200 K. At 120 K the presence of molecular ethylene is indicated by the appearance of the RhC₂H₄⁺ cluster ion (131 amu), whereas also C₂H₄ fragmentation products are observed, e.g. H+ (1 amu), RhC+ (115 amu), Rh₂C⁺ (218 amu), and Rh₂C₂H₂⁺ (232 amu). Atomic nitrogen is indicated by the presence of the Rh₂N⁺ cluster ion (220 amu). Heating to 275 K results in the conversion of ethylene to ethylidyne (CCH₃). This is illustrated in the spectra by the disappearance of the RhC₂H₄⁺ cluster ion and the appearance of the CH₃⁺ ion (15 amu) and its cracking products (14, 13, 12 amu), which are representative for the methyl group in ethylidyne.²¹ The spectrum of the surface at 450 K shows that all the ethylidyne has decomposed and that the surface still contains some hydrogen, reflected by the H⁺ signal (1 amu), most probable as CH_x species. Formation of surface CN is illustrated by the appearance of the Rh₂CN⁺ cluster ion (232 amu) when the surface is heated to 600 K. Note that the surface CN appears only in the Rh₂CN⁺ cluster ion and that the RhCN⁺ cluster ion is not observed. The spectrum of the surface heated to 900 K indicates that all CN has disappeared, either by decomposition or by desorption as HCN, and that the only surface species remaining is (carbidic) carbon, as indicated by the Rh₂C⁺ and RhC⁺ signals.

Kinetics of CN Formation. Temperature-programmed secondary ion mass spectrometry (TPSIMS) has been used to study the kinetics of CN formation on the Rh(111) surface. In contrast to many other surface spectroscopic techniques, SIMS is very powerful in monitoring the concentrations of both atomic and molecular surface species in real time. Usually, linear relations are obtained between adsorbate concentration and appropriate secondary ion intensity ratios.^{22,23} We have used the Rh₂C⁺/Rh₂⁺, Rh₂N⁺/Rh₂⁺, and Rh₂CN⁺/Rh₂⁺ intensity ratios to monitor the surface coverages of C, N and CN, respectively. Figure 4 shows the TPSIMS results obtained from a Rh(111) surface covered with 0.10 ML of N_{ads} and both a small (0.10 langmuir) and a large (1.00 langmuir) amount of coadsorbed ethylene. The heating rate was 4 K/s in both cases.

For the low ethylene coverage case, no HCN desorption is observed and the CN species formed remain stable on the surface up to approximately 700 K where they start to decompose, as is evidenced by the delayed desorption of N₂; see Figure 1. The formation of CN species starts around 480 K, as is illustrated in Figure 4a by both the increase in the Rh₂-CN⁺/Rh₂⁺ intensity ratio and the concomitant decrease in the Rh₂C⁺/Rh₂⁺ and Rh₂N⁺/Rh₂⁺ intensity ratios. CN formation is completed around 625 K where the Rh₂C⁺/Rh₂⁺ intensity ratio becomes zero, indicating that all atomic carbon has been consumed in CN formation. The finite Rh₂N⁺/Rh₂⁺ signal illustrates the small excess of atomic nitrogen although partial fragmentation of the Rh₂CN⁺ cluster ion also contributes to the 220 amu signal. The slight decrease of the Rh₂CN⁺/Rh₂⁺ intensity ratio between 550 and 600 K might be a consequence of partial CN dimerization since small amounts of C₂N₂ desorb under these conditions; see Figure 1. Decomposition of the CN groups around 800 K is illustrated by the decrease of the Rh₂-

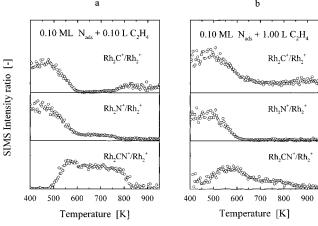


Figure 4. Variation of the Rh₂C⁺/Rh₂⁺, Rh₂N⁺/Rh₂⁺, and Rh₂CN⁺/ Rh₂⁺ SIMS intensity ratios obtained by heating a Rh(111) surface covered with (a) $0.10\ ML\ N_{ads}$ followed by exposure of $0.10\ langmuir$ of C_2H_4 and (b) 0.10 ML N_{ads} followed by exposure of 1.00 langmuir C₂H₄. The heating rate was 4 K/s in both cases.

CN⁺/Rh₂⁺ signal and an accompanied increase of the Rh₂C⁺/ Rh₂⁺ intensity. An increase of the Rh₂N⁺/Rh₂⁺ intensity ratio is not observed, indicating that the atomic nitrogen resulting from decomposition of CN groups desorbs immediately as N₂, in agreement with Figure 1.

For the high ethylene coverage case, shown in Figure 4b, the situation is more complex since CN formation and HCN desorption proceed at the same time. The decrease of the atomic nitrogen and carbon coverages due to CN and HCN formation is still illustrated by the decrease of the Rh₂N⁺/Rh₂⁺ and Rh₂C⁺/ Rh₂⁺ intensity ratios. However, the Rh₂C⁺/Rh₂⁺ intensity does not drop to zero, indicative for an excess of atomic carbon. Interpretation of the Rh₂CN⁺/Rh₂⁺ signal is complicated since it may contain a contribution of the Rh₂C₂H₂⁺ cluster ion. Ethylidyne decomposition has been found to be a strong coverage-dependent process;²⁰ therefore retention of CC bonds up to 500 K is conceivable in the case of high coverages. This explains the nonzero intensity of the 232 amu signal at 400 K. The decrease of the Rh₂CN⁺/Rh₂⁺ intensity above 600 K indicates a decrease of the CN coverage, most probably by hydrogenation to HCN, which desorbs consecutively.

Evidently, low coverages of Nads and C2H4,ads, enabling the hydrocarbon to decompose into elementary carbon at temperatures below the onset of CN formation, give the simplest reaction situation, and hence we have chosen these conditions to determine the kinetic parameters for CN formation. To this end, we have coadsorbed 0.05 ML of atomic nitrogen and 0.025 ML of ethylene, so that, after ethylene decomposition, atomic nitrogen and carbon are present in equal amounts. The low coverage ensures that ethylene has fully decomposed to carbon before CN formation starts.²⁰ If we furthermore assume that $\theta_{\rm C}$ and $\theta_{\rm N}$ are proportional to the Rh₂C⁺/Rh₂⁺ and Rh₂N⁺/Rh₂⁺ SIMS intensity ratios, respectively, which is a reasonable assumption at low coverages, 17,20,22 we can determine the CN formation rate from the decrease of the atomic nitrogen and carbon coverages during a temperature-programmed SIMS

In principle, the CN formation rate can also be derived from the increase of the Rh₂CN⁺/Rh₂⁺ SIMS intensity ratio. If it is assumed that all atomic nitrogen and carbon react to cyanide, the ultimate CN coverage equals 0.05 ML, which could be used to calibrate the Rh₂CN⁺/Rh₂⁺ SIMS intensity ratio. However, it is not clear if the correlation between the CN coverage and the Rh₂CN⁺/Rh₂⁺ SIMS intensity ratio is linear over the entire coverage range. Another complicating factor is that CN may

dimerize on the surface, which also hinders interpretation. For this reason we have primarily used the decrease of the atomic carbon and nitrogen coverages to determine the CN formation

Figure 5a shows the variation of the atomic nitrogen, atomic carbon and cyanide coverage versus the temperature when a surface containing 0.05 ML of atomic nitrogen and 0.05 ML of carbon is heated at 4 K/s. Assuming a homogeneous distribution of C and N on the surface, the rate of reaction can

$$-\frac{\mathrm{d}\theta_{\mathrm{C}}}{\mathrm{d}t} = -\frac{\mathrm{d}\theta_{\mathrm{N}}}{\mathrm{d}t} = \frac{\mathrm{d}\theta_{\mathrm{CN}}}{\mathrm{d}t} = \nu \cdot \mathrm{e}^{-E_{\mathrm{act}}/RT} \cdot \theta_{\mathrm{C}} \cdot \theta_{\mathrm{N}} \tag{1}$$

We find that the experimental results are well described by a preexponential factor and activation energy of 10¹¹ s⁻¹ and 111 kJ/mol, respectively, as shown by the solid lines in Figure 5a. However, reasonable fits could also be obtained by assuming a preexponential factor of 109 s⁻¹ and an activation energy of 91 kJ/mol or a preexponential factor of 10¹³ s⁻¹ and an activation energy of 131 kJ/mol; see dashed lines in Figure 5a.

The upper part of Figure 5a shows a comparison between the CN coverage as calculated from eq 1 (lines) and the CN coverage as determined from the Rh₂CN⁺/Rh₂⁺ SIMS intensity ratio (small circles). We have assumed a linear correlation between θ_{CN} and the Rh₂CN⁺/Rh₂⁺ SIMS intensity ratio, by which good agreement between measured and calculated CN coverages could be obtained for small CN coverage. However, for higher CN coverages the amount of surface cyanide as determined from the Rh₂CN⁺/Rh₂⁺ SIMS intensity ratio is underestimated, which might be a consequence of a nonlinear relation between the CN coverage and the Rh₂CN⁺/Rh₂⁺ SIMS intensity ratio but might also be caused by dimerization of CN groups.

In an attempt to discriminate between preexponential factor and the activation energy, we have varied the heating rate. Figure 5b shows the decrease of the atomic carbon coverage for heating rates of 2, 4, and 10 K/s, starting from a surface covered with 0.10 ML of atomic nitrogen and carbon. The atomic nitrogen coverage showed the same behavior as the atomic carbon coverage and is therefore not shown. The best fit results are obtained for a preexponential factor and activation energy of 10¹¹ s⁻¹ and 111 kJ/mol (solid lines in Figure 5b), and the dashed lines show the results for parameter sets of 10⁹ s⁻¹ and 91 kJ/mol and 10¹³ s⁻¹ and 131 kJ/mol. Thus, we take $\nu=10^{11\pm1}$ s⁻¹ and E_{act} =111 \pm 10 kJ/mol as

the most probable kinetic parameters for CN formation.

Kinetics of CN Decomposition. The kinetic parameters for the cyanide decomposition have been determined in two independent ways. First, the CN decomposition rate was determined indirectly from the N2 desorption rate, which is possible since desorption of N2 is rate limited by cyanide decomposition. Second, the CN decomposition rate was derived from the decrease of the cyanide surface coverage as measured during a temperature-programmed SIMS experiment.

Figure 6a shows a comparison between the N2 desorption rate and the Rh₂CN⁺/Rh₂⁺ SIMS intensity ratio obtained from a Rh(111) surface covered with 0.10 ML of N_{ads} and 0.05 ML of C₂H₄ when heated at 10 K/s. N₂ desorption between 630 and 750 K is accompanied only by a slight decrease in the Rh₂-CN⁺/Rh₂⁺ SIMS intensity ratio. Part of the N₂ desorption in this temperature range might be associated with recombination of atomic nitrogen that has not reacted with CN. However, the increase of the N₂ desorption rate around 700 K cannot be explained by atomic nitrogen recombination and is attributed to CN decomposition. The absence of a significant decrease

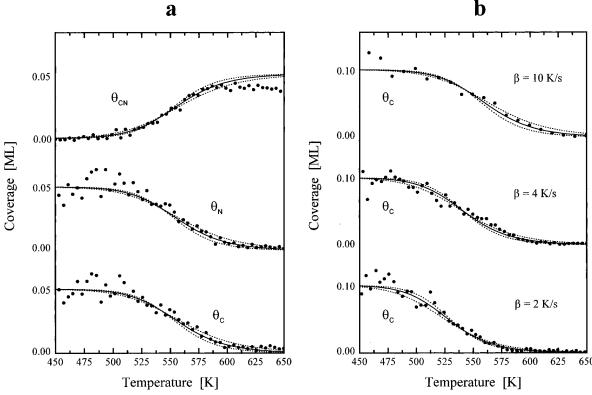


Figure 5. (a) Change of the surface coverages of C, N, and CN versus temperature as derived from the SIMS Rh₂C⁺/Rh₂⁺, Rh₂N⁺/Rh₂⁺, and Rh₂CN⁺/Rh₂⁺ intensity ratios, respectively. The initial N and C coverages were 0.05 ML and the heating rate was 4 K/s. (b) Change of the atomic carbon surface coverage for various heating rates. In both figures the solid lines represent fits using $\nu=10^{11}~{\rm s}^{-1}$ and $E_{\rm act}=111~{\rm kJ/mol}$, while the dashed lines represent fits for $\nu = 10^9 \text{ s}^{-1}$ and $E_{act} = 91 \text{ kJ/mol}$ and $\nu = 10^{13} \text{ s}^{-1}$ and $E_{act} = 131 \text{ kJ/mol}$.

of the Rh₂CN⁺/Rh₂⁺ SIMS intensity ratio due to a decrease of the CN coverage is probably the result of the nonlinearity of the Rh₂CN⁺/Rh₂⁺ SIMS intensity ratio versus the CN coverage. On the high-temperature side of the N₂ desorption peak where the CN coverage is small, the Rh₂CN⁺/Rh₂⁺ SIMS intensity decreases rapidly with proceeding N₂ desorption; note that N₂ desorption finishes when the Rh₂CN⁺/Rh₂⁺ SIMS intensity ratio becomes zero, around 870 K.

Application of the Redhead equation²⁴ to the reaction-limited N₂ desorption state with a peak maximum at 792 K (see Figure 6a) yields an activation energy for CN decomposition of 203 kJ/mol, on the assumption of a preexponential factor of 10¹³

Figure 6b shows the formation and decomposition of surface cyanide as determined from a temperature-programmed SIMS experiment, starting from a surface covered with 0.05 ML of atomic nitrogen and carbon. The heating rate was 4 K/s. The cyanide formation that starts around 500 K has already been discussed in Figure 5a; the solid line shows the fit with a preexponential factor and activation energy of $10^{13} \, \mathrm{s}^{-1}$ and 111kJ/mol, respectively. For these low coverages the decrease of the Rh₂CN⁺/Rh₂⁺ SIMS intensity ratio between 600 and 750 K is more pronounced than in Figure 6a. To determine the CN decomposition rate from the decrease of the CN coverage, we have only considered the temperature range between 700 and 850 K, where a linear correlation between the CN coverage and the Rh₂CN⁺/Rh₂⁺ SIMS intensity ratio is most probable. The solid line shows a fit for the CN decomposition based on

$$-\frac{\mathrm{d}\theta_{\mathrm{CN}}}{\mathrm{d}t} = \nu \cdot \mathrm{e}^{-E_{\mathrm{act}}/RT} \cdot \theta_{\mathrm{CN}} \tag{2}$$

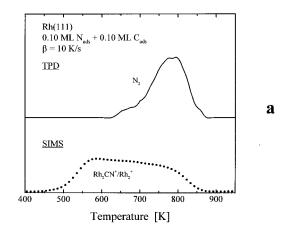
and a preexponential factor and activation energy of 10¹³ s⁻¹ and 210 kJ/mol. These kinetic parameters are in good agree-

ment with those determined by Redhead's method for the N₂ desorption maximum, and therefore we take $\nu = 10^{13\pm1} \, \mathrm{s}^{-1}$ and $E_{\rm act} = 210 \pm 15 \text{ kJ/mol}$ as the most probable parameters for CN decomposition.

Work Function Measurements. Surface reactions can also be followed in a more indirect way by measuring changes in the work function, which is 5.60 eV for the clean Rh(111) surface.²⁵ Figure 7 shows the work function change with respect to the clean surface after deposition of 0.10 ML of N_{ads}, coadsorption of 0.05 ML of C₂H₄ at 120 K, and heating to the indicated temperatures. Except for the adsorption layer at 120 K, all work function measurements were done at 200 K. Deposition of 0.10 ML of atomic nitrogen results in a slight work function increase of approximately +0.03 eV; coadsorption of the C₂H₄ causes a work function drop of -0.16 eV to a value of -0.13 eV with respect to the clean surface. Formation of ethylidyne by heating to 200 K and further heating to 300 K does not result in a measurable work function change. At 400 K, where all ethylidyne has decomposed, the work function has increased to +0.02 eV. Formation of CN on the surface is accompanied by a work function increase between 400 and 500 K. Between 500 and 700 K where CN is a stable surface species, a work function increase of +0.22 eV is measured. Heating to 800 K results in the decomposition of the CN species and the work function change drops to zero again, characteristic of the clean Rh(111) surface.

Discussion

Reduction of NO by hydrocarbons, of interest in automotive exhaust catalysis, gives rise to a large number of surface reactions that lead to the desorption of many products, e.g. H₂, H₂O, N₂, CO, CO₂, HCN, and C₂N₂. The complexity of this reaction precludes meaningful kinetic analysis. The aim of the



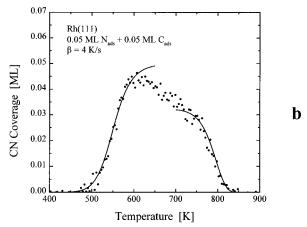


Figure 6. (a) Comparison between the N_2 desorption rate and the Rh_2 - CN^+/Rh_2^+ SIMS intensity ratio as measured for a Rh(111) surface covered with 0.10 ML of N_{ads} and 0.05 ML of C_2H_4 when heated at 10 K/s. (b) Determination of the CN decomposition rate from the decrease of the CN surface coverage. The solid line represents a fit based on a preexponential factor and activation energy of 10^{13} s⁻¹ and 210 kJ/mol, respectively.

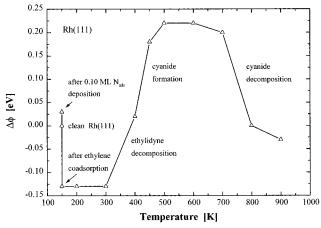


Figure 7. Change of the work function with respect to the clean Rh-(111) surface as a consequence of N_{ads} and C_2H_4 adsorption and heating to the indicated temperatures. All measurements were done at 200 K.

present work is therefore to simplify the situation by highlighting the reaction pathways of atomic nitrogen and ethylene in the absence of oxygen. The results presented here demonstrate the feasibility of the approach, as kinetic parameters could be derived for the formation and decomposition of adsorbed CN species.

Excluding the decomposition of ethylene, which has been extensively discussed,²⁰ the following reactions have been found relevant in this study

$$C_{ads} + N_{ads} \rightarrow CN_{ads}$$
 $T \sim 480 - 625 \text{ K}$ (3)

$$\mathrm{CN}_{\mathrm{ads}} + \mathrm{CH}_{\mathrm{x,ads}} \rightarrow \mathrm{HCN}^{\uparrow} + \mathrm{CH}_{\mathrm{x-1,ads}}$$

$$T \sim 500 - 750 \, \mathrm{K} \qquad (4)$$

$$N_{ads} + CH_{ads} \rightarrow HCN^{\uparrow}$$
 $T \sim 500-750 \text{ K}$ (5)

$$CN_{ads} + CN_{ads} \rightarrow C_2N_2^{\uparrow}$$
 $T \sim 680 - 820 \text{ K}$ (6)

$$\text{CN}_{\text{ads}} \rightarrow {}^{1}/_{2}\text{N}_{2}^{\dagger} + \text{C}_{\text{ads}} \qquad T \sim 700 - 850 \text{ K}$$
 (7)

$$N_{ads} + N_{ads} \rightarrow N_2 \uparrow$$
 $T \sim 550 - 750 \text{ K}$ (8)

where reactions 3 and 6-8 are thought to be elementary and reactions 4 and 5 may be composite in nature.

The reaction between atomic carbon and nitrogen to CN, (3), could conveniently be studied in the low coverage regime, where ethylene decomposes to fully dehydrogenated carbon below the temperature where CN starts to form. The rate of reaction 3 is straightforwardly described by an expression of the form $r_{\rm CN} = k \cdot \theta_{\rm N} \cdot \theta_{\rm C}$ with an activation energy of 111 ± 10 kJ/mol and a preexponential of $10^{11\pm1}$ s⁻¹. Such parameters are fully consistent with the notion of reaction 3 being an elementary step.²⁹ The onset temperature for cyanide formation, 480 K, is similar to the 450 K reported by DeLouise and Winograd¹⁵ for the onset of CN formation on Rh(331) by reaction between NO and carbon

Formation of HCN almost certainly involves CH_x species, as single H-atoms have desorbed at 500 K. As known from previous work from several laboratories,²⁰ hydrocarbon fragments may still contain hydrogen, especially at increasing coverages, where the decomposition of ethylene and other alkenes is progressively retarded. Hence, we propose two possibilities for HCN formation, reactions 4 and 5, which may, but do not have to be, elementary reactions. For example, we cannot exclude that reaction 4 proceeds by CH_x decomposition, immediately followed by a reaction of the H-atom with a previously formed CN group. Although desorption of H₂ is not observed, one could argue that if the rate-determining step in the overall reaction 4 is CH_x decomposition, the surface concentration of H-atoms is so low in comparison to that of CN that H₂ formation is insignificant. Clear evidence for the occurrence of reaction 4 is provided by Figure 5b, which shows that the surface coverage of CN species decreases while HCN evolves in the gas phase. Unfortunately, we have no such definite proof for reaction 5, nor any evidence to discard it, the major problem being that SIMS does not readily distinguish between adsorbed CH and C species.

Interestingly, Schmidt and co-workers¹² reported that the decomposition of CH₃NH₂ on Rh(111) results in HCN desorption around 430 K, i.e. some 70 K below the temperatures where HCN forms in this study. This confirms that HCN desorption is limited by the formation of HCN through either of the reactions 4 or 5.

Cyanogen desorption, around 750 K, has also been observed in C_2N_2 adsorption studies^{11,12} and has been attributed to recombination of CN groups. Since we start from atomic nitrogen and ethylene, we can be certain that C_2N_2 formation has to precede desorption. We observe an optimum in the C_2N_2 selectivity for an ethylene exposure where the surface concentration of cyanide maximizes. The observation of an optimum can be understood from the fact that, for the lowest ethylene coverage, surface carbon is deficient and CN decomposition is

favorable, while at high ethylene coverages HCN formation and desorption becomes competitive to C_2N_2 formation. The correlation of the C_2N_2 selectivity with the cyanide coverage sustains the assignment that the C_2N_2 desorption state at 750 K is reaction limited by dimerization of surface cyanide groups.

CN species start to decompose around 700 K. The reaction could be followed by SIMS (Figure 7) and the kinetics is adequately described by a first-order rate equation with an activation energy of 210 \pm 15 kJ/mol and a preexponential of $10^{13\pm1}~\text{s}^{-1}$. N-atoms released in this reaction recombine and desorb instantaneously. The reaction-limited N_2 desorption state with a maximum at 800 K has also been observed in C_2N_2 and CH_3NH_2 decomposition experiments. 11,12

The increase in the work function as a consequence of CN formation indicates that the cyanide is present as a negatively charged species, which is a common feature for cyanides adsorbed on group VIII metals. Although we have no direct information about the bonding type of the cyanide, the SIMS results suggest that the cyanide species is most probably adsorbed on a site involving more than one Rh atom. Brown and Vickerman²³ have shown that the binding site of CO is reflected by the relative intensities of 1, 2, and 3-fold metal-CO clusters. Linear CO adsorption displays itself by dominance of the single metal-CO clusters while bridge bonded CO manifests itself by larger intensities of the 2- and 3-fold metal-CO clusters. If we draw the analogy between CO and CN, it is noteworthy that Rh(CN)⁺ cluster ions are entirely absent and only Rh₂CN⁺ cluster ions are observed (for sensitivity reasons Rh₃CN⁺ cluster ions could not be detected). HREELS and NEXAFS measurements give clear evidence that CN is adsorbed parallel to the surface on Pd(111).^{9,26} Flat-lying CN is neither observable by EELS in the dipole scattering mode nor by IR spectroscopy. This might be the reason this species was overlooked in adsorption and decomposition studies of CH₃-NC on both Al₂O₃ supported Rh and Rh(111).^{27,28} The absence of the Rh(CN)⁺ cluster ion in the SIMS spectra could be the consequence of a flat-lying species, however, the exact bonding nature of the CN species needs further investigation.

Conclusions

The selectivity of the reaction between atomic nitrogen and ethylene depends strongly on the ethylene coverage. For small ethylene coverages, ethylene fully decomposes to carbon, which subsequently reacts with atomic nitrogen to a surface cyanide species. The kinetics of CN formation from atomic carbon and nitrogen could best be described by a preexponential and an activation energy of $10^{11\pm1}$ s⁻¹ and 111 ± 10 kJ/mol, respectively. In the absence of surface hydrogen, CN groups are stable up to \sim 700 K. CN decomposition results in a reaction-limited

 N_2 desorption state with a maximum at 792 K and can best be described by a preexponential factor and activation energy of $10^{13\pm1}$ s⁻¹ and 210 ± 15 kJ/mol, respectively. For high ethylene coverages, ethylene decomposition is retarded and HCN formation in the temperature range between 500 and 650 K by reaction between atomic nitrogen and CH_x becomes the preferential reaction pathway. The optimum in the cyanogen selectivity ($\approx 3\%$) corresponds to a maximum in the cyanide surface coverage, and the desorption at 750 K is reaction limited by, most probably, dimerization of CN groups. Surface cyanide is present as negatively charged, presumably flat-lying, species.

References and Notes

- (1) McKetta, J. J. Encyclopedia of chemical processing and design; M. Dekker: New York, 1988; Vol. 27, p 7.
- (2) Bamwenda, G. R.; Obuchi, A.; Ogata, A.; Mizuno, K. Chem. Lett. 1994, 2109.
- (3) Obuchi, A.; Ohi, A.; Nakamura, M.; Ogata, A.; Mizuno, K.; Ohuchi, H. *Appl. Catal. B* **1993**, *2*, 71.
 - (4) Burch, R.; Millington, P. J. Catal. Today 1995, 26, 185.
 - (5) Burch, R.; Watling, T. C. Catal. Lett. 1996, 37, 51.
 - (6) Hasenberg, D.; Schmidt, L. D. J. Catal. 1985, 91, 116.
- (7) Hemminger, J. C.; Muetterties, E. L.; Somorjai, G. A. J. Am. Chem. Soc. 1979, 101, 62.
- (8) Kingsley, J. R.; Dahlgren, D.; Hemminger, J. C. Surf. Sci. 1984, 139, 417.
- (9) Kordesch, M. E.; Stenzel, W.; Conrad, H. Surf. Sci. 1987, 186, 601.
 - (10) Gudde, N. J.; Lambert, R. M. Surf. Sci. 1983, 124, 372.
 - (11) Solymosi, F.; Bugyi, L. Surf. Sci. 1984, 147, 685.
- (12) Hwang, S. Y.; Kong, A. C. F.; Schmidt, L. D. J. Phys. Chem. 1989, 93, 8327.
- (13) Hwang, S. Y.; Kong, A. C. F.; Schmidt, L. D. J. Phys. Chem. 1989, 93, 8334.
 - (14) Wagner, W. L.; Schmidt, L. D. Surf. Sci. 1991, 257, 113.
 - (15) DeLouise, L. A.; Winograd, N. Surf. Sci. 1985, 154, 79.
- (16) Van Hardeveld, R. M.; Schmidt, A. J. G. W.; Niemantsverdriet, J. W. Catal. Lett. 1996, 41, 125.
- (17) Borg, H. J.; Reijerse, J. F. C-J. M.; Van Santen, R. A.; Niemantsverdriet, J. W. J. Chem. Phys. **1994**, 101, 10052.
- (18) Van Hardeveld, R. M.; Van Santen, R. A.; Niemantsverdriet, J. W. J. Phys. Chem. **1997**, 101, 998.
- (19) Belton, D. N.; DiMaggio, C. L.; Ng, K. Y. S. J. Catal. 1993, 144, 273
- (20) Borg, H. J.; Van Hardeveld, R. M.; Niemantsverdriet, J. W. J. Chem. Soc., Faraday Trans. 1995, 91, 3679 and references therein.
 - (21) Creighton, J. R.; White, J. M. Surf. Sci. 1983, 129, 327.
- (22) Borg, H. J.; Niemantsverdriet, J. W. In *Catalysis: a Specialist Periodical Report*; Royal Society of Chemistry, Cambridge, 1994; Vol 11, p 1.
 - (23) Brown, A.; Vickerman, J. C. Surf. Sci. 1983, 124, 267.
 - (24) Redhead, P. A. Vacuum 1962, 12, 203.
- (25) Castro, G. R.; Busse, H.; Schneider, U.; Janssens, T.; Wandelt, K. *Phys. Scr.* **1992**, *T41*, 208.
 - (26) Wirgin, A.; Lopez-Rios, T. Opt. Commun. 1984, 48, 416.
- (27) Cavanagh, R. R.; Yates, J. T., Jr. J. Chem. Phys. 1981, 75, 1551.
- (28) Semancik, S.; Haller, G. L.; Yates, J. T. Jr. J. Chem. Phys. 1983, 78, 6970.
- (29) Van Santen, R. A.; Niemantsverdriet, J. W. Chemical Kinetics and Catalysis; Plenum Press: New York, 1995.