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Cyanide intermediates in catalytic reduction of NO by C_2H_4 on rhodium (111)

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Temperature programmed reaction spectroscopy and secondary ion mass spectrometry (SIMS) have been applied to study reactions of NO and C_2H_4 coadsorbed on Rh(111). As expected, H_2O, CO_2, and N_2 are the main products at low C_2H_4 coverages, but at higher coverages H_2, HCN, CO, and NO, and even some C_2N_2 evolve as well. Static SIMS indicates the formation of a large supply of adsorbed CN species, part of which desorbs as HCN, while the remainder decomposes and is responsible for delayed formation of N_2. For the highest C_2H_4 coverages, the majority of the nitrogen atoms in the initially adsorbed NO desorbs as HCN. © 1997 American Vacuum Society.

I. INTRODUCTION

Hydrocarbons play a significant role in the removal of NO from automotive exhaust gases by the three-way catalyst. The cracking of gasoline in the engine is responsible for the presence of a number of different hydrocarbons, such as methane, acetylene, ethylene, benzene, and toluene. Unsaturation hydrocarbons decompose on the surface of the noble metal particles in the three-way catalyst and, thus, provide a source of H and C atoms that are available for reaction with the other exhaust constituents. Here we focus on reactions of NO and ethylene on Rh(111).

The dissociative adsorption of NO on Rh(111) and the selectivity towards formation of N_2 are strongly affected by the extent to which the surface is occupied. At low NO coverages (below 0.2 ML), all NO dissociates around room temperature, and N_2 is seen to desorb between 500 and 700 K. If the NO coverage is higher than about 0.2 ML, part of the NO desorbs, and N_2 desorbs in two states, one at low temperature showing first-order desorption kinetics, and the other the normal second-order desorption channel of N_2, which, however, is strongly affected by repulsive interactions with N and O atoms. Secondary ion mass spectrometry (SIMS) experiments showed that NO dissociation is retarded to temperatures where NO desorption takes place. This coverage-dependent effect in the dissociation rate of NO has been attributed to an ensemble requirement of a dissociating NO molecule. As a result, the dissociation at fully occupied surfaces is retarded to the temperatures where some NO desorbs, after which dissociation of remaining NO and desorption of a part of the N_2 follow instantaneously.

Also the decomposition of ethylene has extensively been studied, in particular on Pt and Rh (Refs. 4–6). In brief, ethylene adsorbs molecularly on rhodium at low temperatures, say around 100 K. At low coverages, ethylene reacts to vinyl, —CH=CH_2 and a H atom, while at all coverages the well-known species ethylidyne, C_2H_3 forms around 180 K. At about 300 K the ethylidyne decomposes further to acetylene (CCH), CH, and carbidic C atoms. The decomposition reaction is retarded at higher coverages.

Formation of HCN is obviously an unwanted reaction of N atoms in the three-way catalyst. It becomes feasible when nitrogen and hydrocarbon residues are present on the surface. In this article we describe reactions between NO and ethylene on the (111) surface of rhodium. We use temperature programmed reaction spectroscopy (TPRS) to monitor desorbing product gases and secondary ion mass spectrometry to explore reactions on the surface. The results indicate that considerable amounts of cyanide groups form on the surface, part of which give rise to HCN formation, while the remaining CN delays the desorption of N_2 to higher temperatures.

II. EXPERIMENT

Experiments were done in an ultrahigh vacuum (UHV) system (base pressure around 1×10^−10 mbar) equipped with a Leybold SSM 200 quadrupole mass spectrometer for temperature programmed desorption (TPD) and static SIMS (SSIMS) measurements, as described elsewhere. 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 up to 1500 K. Temperatures were measured with a Chromel–Alumel thermocouple spot welded on the backside of the crystal. Small amounts of bulk impurities, such as sulphur, chlorine, and boron were removed by cycles of argon sputtering (1.5 keV, 5 μA/cm^2) at 900 K and annealing to 1400 K. Carbon was removed by annealing the crystal in 2×10^−8 mbar O_2 by slowly varying the temperature between 900 and 1100 K. Oxygen was removed from the surface by annealing to 1425 K. Ethylene (Messer Griesheim, 99.95% pure) and NO (Messer Griesheim, 99.5% pure) were used without further purification, gas exposures are reported in langmuirs (1 L=1.33×10^−6 mbar s); coverages are reported in monolayers (ML, number of adsorbates per Rh surface atom).
III. RESULTS AND DISCUSSION

A. NO+ethylene at low coverage

First, we describe the reaction between adsorbed NO and ethylene at low coverage. Figure 1 shows TPD and SIMS spectra obtained during heating of the Rh\textsubscript{111} surface covered with 0.10 ML of NO and 0.03 ML of ethylene. The upper half of Fig. 1 shows that H\textsubscript{2}O, CO\textsubscript{2}, and N\textsubscript{2} are the main desorbing products, along with small amounts of H\textsubscript{2} and some CO. The mass 28 signal consists of two peaks, the one around 500 K being characteristic of CO\textsubscript{2} as appears from checking the masses 12, 14, and 16 and the other representing N\textsubscript{2}. Note that part of the CO signal is a fragment of CO\textsubscript{2} (roughly 10% of CO\textsubscript{2} cracks to CO in the mass spectrometer), and that the actual amount of desorbing CO is small.

The TPSIMS intensities in the lower half of Fig. 1 reflect reactions on the surface during heating. In order to compensate at least partially for effects due to changes in work function during decompositions and reactions on the surface, it is customary to consider intensity ratios such as RhC\textsubscript{2}H\textsubscript{4}\textsuperscript{+}/Rh\textsuperscript{+}, which often quite closely correlate with adsorbate coverage.\cite{6}

First, the RhC\textsubscript{2}H\textsubscript{4}\textsuperscript{+}/Rh\textsuperscript{+} signal in Fig. 1, indicative for adsorbed ethylene, shows that ethylene starts to decompose at about 130 K. From previous work of Borg et al.\cite{6} we know that ethylene when present in low coverages on Rh\textsubscript{111}, reacts at about 130 K to vinyl, --CH\textsubscript{2}CH\textsubscript{3}, and a H atom. The vinyl rearranges at about 180 K to ethylidyne, C–CH\textsubscript{3}. The latter is in principle visible by a CH\textsubscript{3} signal, but at the coverages employed in Fig. 1, the intensity is very weak and has, therefore, not been included.

The Rh\textsubscript{2}N\textsuperscript{+} ion monitors the dissociation of adsorbed NO, which sets in at about 275 K. N atoms remain on the surface until desorption of N\textsubscript{2} begins just above 500 K. The other ion, Rh\textsubscript{2}CN\textsuperscript{+}, at 232 amu, is included for comparison with experiments to be described next. The intensity of this mass signal at low temperatures is due to the adsorbed ethylene, which produces a Rh\textsubscript{2}C\textsubscript{2}H\textsubscript{2} fragment at the same mass.

Thus, at low coverages NO and ethylene decompose as if they were on the Rh\textsubscript{111} surface separately. The reaction products are mainly the expected H\textsubscript{2}O, CO\textsubscript{2}, and N\textsubscript{2}, with small amounts of H\textsubscript{2} and CO formed as well.

B. NO+ethylene at higher coverage

A TPD/TPSIMS experiment done with 0.20 ML of NO coadsorbed with 0.12 ML of ethylene, shown in Fig. 2, illustrates the reaction pathways occurring at higher coverages.
The TPD spectra in the upper half of Fig. 2 reveal that in addition to N\textsubscript{2}, CO\textsubscript{2}, and H\textsubscript{2}O, also significant amounts of H\textsubscript{2}, NO, CO, and HCN form. Traces of C\textsubscript{2}N\textsubscript{2} (not shown) are observed as well. Following the proper fragmentation signals at 12, 14, 16, and 27 amu enables interpretation of the mass 28 signal; it appears that ethylene does not desorb in this particular experiment, that the peaks between 400 and 600 K are due to CO and that the peak above 700 K is caused by desorption of N\textsubscript{2}.

Static SIMS data are given in the lower half of Fig. 2; we discuss the trends from low to high temperature. The first surface reaction that appears during heating of C\textsubscript{2}H\textsubscript{4} and NO is the conversion of ethylene to ethylidyne, CCH\textsubscript{3}, and H atoms, between 190 and 220 K.\textsuperscript{6} The SIMS spectra in Fig. 2 indicate the conversion of ethylene by a decrease of the Rh\textsubscript{2}C\textsubscript{2}H\textsubscript{4}/Rh\textsuperscript{+} ratio and the accompanied formation of ethylidyne by the appearance of the methyl secondary ion, CH\textsubscript{3}\textsuperscript{+}. The fact that we do not observe the ethylene-to-vinyl transition visible by the disappearance of the RhC\textsubscript{2}H\textsubscript{4} signal in Fig. 1 is consistent with earlier work that showed that this reaction is strongly retarded at higher coverages.\textsuperscript{8} The H atoms formed in the ethylene—ethylidyne reaction start to desorb around 270 K.

Just below 300 K, NO dissociation sets in, as reflected by the growth of the Rh\textsubscript{2}N\textsuperscript{+} signal characteristic of N atoms, and the evolution of H\textsubscript{2}O, which is reaction limited above 200 K on Rh(111).\textsuperscript{9} NO dissociation occurs in two steps, the first between roughly 300 and 350 K, after which the Rh\textsubscript{2}N\textsuperscript{+} intensity reaches a short plateau, and the second above 400 K, as can be inferred from a further rise in the Rh\textsubscript{2}N\textsuperscript{+} intensity and the appearance of additional peaks in the desorption of CO\textsubscript{2} and H\textsubscript{2}O, as we discuss in more detail below.

The decomposition of ethylidyne, seen by the decrease of the CH\textsubscript{3} intensity in SIMS, falls in the temperature range of approximately 300–380 K, and is accompanied by the formation of H atoms, which either desorb as H\textsubscript{2} or react with O atoms and a second H atom to H\textsubscript{2}O, which desorbs instantaneously. H\textsubscript{2} desorption terminates at about 450 K. Note, however, that the surface still contains hydrogen, most probably present in the form of carbonaceous species, as H\textsubscript{2}O and HCN continue to desorb to almost 600 and 700 K, respectively.

Oxidation of C atoms appears to begin at 380 K, as the growth of a RhCO\textsuperscript{+} in SIMS, and the more or less simultaneous desorption of CO\textsubscript{2} indicate. Apparently, the reaction between adsorbed CO and O is not sufficiently rapid to prevent accumulation of CO on the surface, which is probably caused by lack of sufficient O atoms. CO desorption is seen above 450 K both in TPD and in SIMS, in agreement with the literature of CO on Rh (111).\textsuperscript{10,11} Also in this region, 450–520 K, is the desorption of NO. Following earlier work, we propose that this NO desorbs because the surface is to a large extent occupied, implying that the relatively large ensembles of free rhodium atoms necessary for NO dissociation are not available.\textsuperscript{2,3} Hence, NO desorbs as soon as the temperature is high enough to permit this. Interestingly, the desorption temperature of NO is significantly (i.e., about 70 K) higher than if NO is the only adsorbate.\textsuperscript{2,7} The difference is that, in the latter case, the NO molecules desorb out of a repulsive environment of NO, N, and O atoms, while in the present case the environment contains carbonaceous species as well. To what extent the shift in NO desorption to higher temperatures is caused by reduced repulsion or by increased attraction by carbonaceous species is not clear, however.

The SIMS data in Fig. 2 strongly suggest that a large inventory of cyanide groups forms on the surface between 450 and 550 K. First, the Rh\textsubscript{2}CN\textsuperscript{+} intensity increases strongly and second, the intensities of both Rh\textsubscript{2}N\textsuperscript{+} and Rh\textsubscript{2}C\textsuperscript{+}, characteristic of atomic nitrogen and carbon at these temperatures, decrease. Although the Rh\textsubscript{2}C\textsuperscript{+} is observed as a fragment of adsorbed C\textsubscript{2}H\textsubscript{4} species as well, it is very likely that all C–C bonds have broken at the temperatures where CN groups start to form (i.e., 450 K). The Rh\textsubscript{2}N\textsuperscript{+} intensity falls to a low value reflecting the fragmentation of Rh\textsubscript{2}CN\textsuperscript{+}, while the Rh\textsubscript{2}C\textsuperscript{+} falls practically to zero. Note that the observation of CN on the surface coincides with the onset of the HCN desorption and that CN formation occurs at higher temperatures than CO formation, reflecting that the reaction between carbon and oxygen is preferred above that between carbon and nitrogen atoms.

We do not believe that the cyanide is present as adsorbed HCN, because, first, the SIMS signal of the corresponding Rh\textsubscript{2}HCN\textsuperscript{+} is not observed and second, the irregular leading edge of the HCN desorption trace, starting at 450 K, suggests a reaction limited desorption process. Hwang \textit{et al.} observed a reaction limited HCN desorption state at 430 K starting from methyl amine CH\textsubscript{3}NH\textsubscript{2} on Rh(111).\textsuperscript{12} Part of the cyanide inventory is hydrogenated to HCN between 500 and 650 K, as seen by the desorption of HCN and the decrease in the Rh\textsubscript{2}CN\textsuperscript{+} SIMS signal. Apparently, the adsorbate layer is fully dehydrogenated above 650 K. The cyanide species remain stable until about 720 K where N\textsubscript{2} desorption starts to occur, as evidenced by the N\textsubscript{2} signal in TPD (accompanied by a parallel signal at 14 amu), a decrease in the Rh\textsubscript{2}CN\textsuperscript{+} signal in SIMS and an increase in the Rh\textsubscript{2}C\textsuperscript{+} signal characteristic of adsorbed carbon. The Rh\textsubscript{2}N\textsuperscript{+} ion characteristic of adsorbed N atoms, is not observed, indicating that N\textsubscript{2} desorbs instantaneously. The decrease of the Rh\textsubscript{2}C\textsuperscript{+} signal above 900 K is attributed to the dissolution of carbon into the rhodium crystal.\textsuperscript{13}

\textbf{C. NO+ethylene at saturation coverages}

For comparison with high pressure conditions, we have investigated the reactions between NO and ethylene on a saturated surface for both NO and ethylene enriched cases.

In the NO deficient case, 0.05 ML NO was adsorbed after which the surface was saturated by exposure of 1.0 L C\textsubscript{2}H\textsubscript{4} (in this case, the C\textsubscript{2}H\textsubscript{4}:NO ratio is expected to be at least 4:1). At this fully covered surface, not all ethylene can dissociate as is evidenced by a molecular ethylene desorption state at 210 K in the TPRS experiments. NO desorption was observed and all nitrogen desorbed as HCN. H\textsubscript{2}O formation started at 275 K, in good agreement with the onset of the NO dissociation, and extended to 600 K. Furthermore,
CO formation was favored over CO₂ formation, and large amounts of H₂ desorbed between 250 and 450 K. In order to determine the reaction selectivity in excess NO, we have adsorbed 0.40 ML NO and saturated the surface with ethylene by exposure of 1.00 L. In this case, the NO:C₂H₄ ratio is expected to be at least 5:1! Higher NO coverages were found to inhibit ethylene coadsorption almost entirely. Under these conditions no HCN production is observed and excess NO desorbs in two desorption states at 450 and 480 K, respectively. Due to excess oxygen, ethylene is predominantly oxidized to H₂O and CO₂, and hardly any CO and H₂ desorb. As a consequence of site blocking by NO, part of the ethylene desorbed molecularly at 250 K, which is a significantly higher temperature and might indicate some stabilization of the ethylene by the presence of the NO.

D. Reaction of N atoms and ethylene to HCN

In order to simplify the number of reactions that can occur simultaneously, we have done a series of experiments in which the NO was dissociated and the oxygen removed by hydrogen, before ethylene was coadsorbed. The procedure of making N layers in well-established amounts is described elsewhere.¹⁴

The TPD spectra in Fig. 3 shows a series of N₂, HCN, C₂N₂, and H₂ desorption traces for a Rh(111) surface covered by 0.10 ML of N atoms, coadsorbed with varying amounts of ethylene on Rh(111), measured at a heating rate of 10 K/s. The adsorption temperature was 120 K.

CO formation was favored over CO₂ formation, and large amounts of H₂ desorbed between 250 and 450 K. In order to determine the reaction selectivity in excess NO, we have adsorbed 0.40 ML NO and saturated the surface with ethylene by exposure of 1.00 L. In this case, the NO:C₂H₄ ratio is expected to be at least 5:1. Higher NO coverages were found to inhibit ethylene coadsorption almost entirely. Under these conditions no HCN production is observed and excess NO desorbs in two desorption states at 450 and 480 K, respectively. Due to excess oxygen, ethylene is predominantly oxidized to H₂O and CO₂, and hardly any CO and H₂ desorb. As a consequence of site blocking by NO, part of the ethylene desorbed molecularly at 250 K, which is a significantly higher temperature and might indicate some stabilization of the ethylene by the presence of the NO.

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The TPD spectra in Fig. 3 shows a series of N₂, HCN, C₂N₂, and H₂ desorption traces for a Rh(111) surface covered by 0.10 ML of N atoms and variable amounts of ethylene, coadsorbed at 120 K. For small coverages of ethylene, N₂ and H₂ are the only desorbing products, implying that carbon remains on the surface. Note, however, that the N₂ desorption traces shift to higher temperatures, indicating that part of the N atoms have already reacted to CN with the decomposition products of ethylene (mostly C atoms at these low coverages). Thus, we propose that the leading edge of the N₂ desorption signal represents the recombination of two N atoms on the surface, while at higher temperatures the signal is due to CN decomposition. Between C₂H₄ exposures between 0.1 and 0.50 L, small amounts of C₂N₂ desorb in a reaction limited state with a maximum at 750 K. This desorption state has also been observed by Solymosi and Bugyi,¹⁵ who studied the adsorption and decomposition of C₂N₂ on Rh(111).

At higher ethylene coverages, HCN starts to desorb, until at the highest ethylene doses, HCN is the only N-containing product. The onset of HCN desorption is at 520 K, i.e., at temperatures where H atoms have already desorbed. Hence, HCN formation is a reaction limited event, involving CH₃ species.

Finally, we discuss the kinetic parameters of CN formation on the surface. A Rh(111) surface with 0.05 ML of N ads was exposed to a small dose of ethylene corresponding to 0.05 ML of adsorbed C atoms. This is a coverage regime where ethylene dehydrogenates completely below 500 K, and desorption of HCN and C₂N₂ is not observed. A temperature programmed SIMS experiment was done to monitor the coverages of carbon and CN species through the SIMS Rh₂C⁺/Rh₂ and Rh₂CN⁺/Rh₂ peak intensity ratios. As Fig. 4 shows, a reaction between C atoms and N atoms to adsorbed CN species starts at 500 K and is completed at about 650 K. The data can satisfactorily be fitted with the following rate equation:
\[
\frac{d \theta_C}{dt} = \frac{d \theta_{CN}}{dt} = u \cdot e^{-E_{act}/RT} \cdot \theta_C \cdot \theta_N,
\]

yielding \( E_{act} = 111 \pm 10 \text{ kJ/mol} \) and \( v = 10^{11} \pm 1 \text{ s}^{-1} \), suggesting that this reaction is indeed an elementary one.\(^3\) Similar experiments with higher initial, though equal N and C coverages give the same picture. The formation of CN species is responsible for the retarded desorption of \( \text{N}_2 \), the rate of which is limited by the decomposition of the CN.

IV. CONCLUDING REMARKS

Temperature programmed reactions of NO and \( \text{C}_2\text{H}_4 \) produce a broad spectrum of products. At low \( \text{C}_2\text{H}_4 \) coverages, \( \text{H}_2, \text{H}_2\text{O}, \text{CO}_2, \) and \( \text{N}_2 \) are the dominant products, but as the coverage increases, NO dissociation becomes hindered, and the fraction of NO that does dissociate has a relatively large probability to be trapped in an extensive reservoir of CN species, which forms between 450 and 550 K. For low coverages, this is well above the NO dissociation temperature, and also above the temperature where the C–C bond breaks, hence, we conclude that neither NO dissociation nor C–C bond scission is rate determining and that CN formation from adsorbed C and N atoms has an activation barrier of 111 kJ/mol together with a preexponential of \( 10^{11} \text{ s}^{-1} \). Depending on the availability of H atoms, which are released from hydrocarbon fragments in the temperature range of 500–700 K, CN may be hydrogenated to gas phase HCN. In the absence of hydrogen, the CN species are sufficiently stable to retard the desorption of \( \text{N}_2 \) by some 200 K to the range of 650–850 K. The experiments on the reaction between adsorbed N atoms and ethylene indicate that the selectivity for N to desorb as HCN can be as high as 100%.

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\(^{1}\) R. Impens, in *Catalysis and Automotive Pollution Control*, edited by A. Crucq and A. Frennet (Elsevier Science, Amsterdam, 1987), p. 11.


