

Kinetics of elementary surface reactions studied by static secondary ion mass spectrometry and temperature programmed reaction spectroscopy¹

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Abstract

The application of static secondary ion mass spectrometry (SIMS) in combination with temperature programmed desorption (TPD) or reaction spectroscopy in surface chemistry on metal single crystal surfaces is illustrated with reactions that are relevant in the context of automotive exhaust catalysis on rhodium. In unravelling the complex mechanism of surface reactions between NO and ethylene, TPD detects the evolution of products in the gas phase while secondary ion mass spectrometry (SIMS) monitors processes on the surface in substantial detail. The possibility to derive kinetic parameters of elementary surface reactions from SIMS data is demonstrated with studies on the dissociation of NO and the formation of CN species from N and C atoms. © 1998 Elsevier Science B.V.

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1. Introduction

Catalytic reaction mechanisms always consist of a sequence of elementary steps, most of which occur on the surface of the catalyst. Hence, a complete kinetic description of a catalytic mechanism on the molecular scale can only be given if the kinetic parameters—activation energy, preexponential factor and order of reaction—are known for all the kinetically significant elementary steps. Where in practical catalysis most of the constituent reaction steps

occur inside the catalyst bed in a reactor, surface science offers the opportunity to study many elementary steps in isolation on the surface of a metal single crystal.

Several techniques have the capability to monitor surface reaction steps with a time resolution on the order of a second. Temperature programmed reaction spectroscopy (TPRS) is by far the most popular method, but techniques such as SIMS, pulsed-field or laser desorption, reflection absorption infrared spectroscopy, or even X-ray photoelectron spectroscopy when done on synchrotrons, offer attractive possibilities as well.

The purpose of this paper is to illustrate the usefulness of static SIMS in combination with

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¹ In memory of Brian Bent whose publications and presentations have inspired us greatly.

TPRS. We will discuss examples taken from our own work on surface reactions that are relevant in the context of automotive exhaust catalysis.

2. Static SIMS in surface chemistry

SIMS is by far the most sensitive surface technique, but also the most difficult one to quantify. SIMS is very popular in materials research for making concentration depth profiles and chemical maps of the surface. In surface chemistry, the technique offers the opportunity to monitor reactions of adsorbed molecules. The principle of SIMS (see Fig. 1) is conceptually simple: a primary ion beam (Ar^+ : 0.5–5 keV) is used to sputter atoms, ions and molecular fragments from the surface. The ions among these secondary species can directly be analysed with

a mass spectrometer. The theory behind SIMS, however, is far from simple. In particular, the formation of ions upon sputtering in or near the surface is hardly understood. The interested reader will find a wealth of information on SIMS in the books by Benninghoven et al. [1] and Vickerman et al. [2], while many applications have been described by Briggs and Seah [3]. A review of SIMS in catalysis and surface chemistry has recently been published by Borg and Niemantsverdriet [4].

The advantages of SIMS are its high sensitivity, enabling detection in real time, its ability to detect surface hydrogen atoms and the emission of molecular fragments which often bear tractable relationships with the parent structure on the surface (see Fig. 1). Disadvantages are that secondary ion formation is a poorly understood phenomenon and that quantitation is often difficult. A major drawback is the matrix effect:

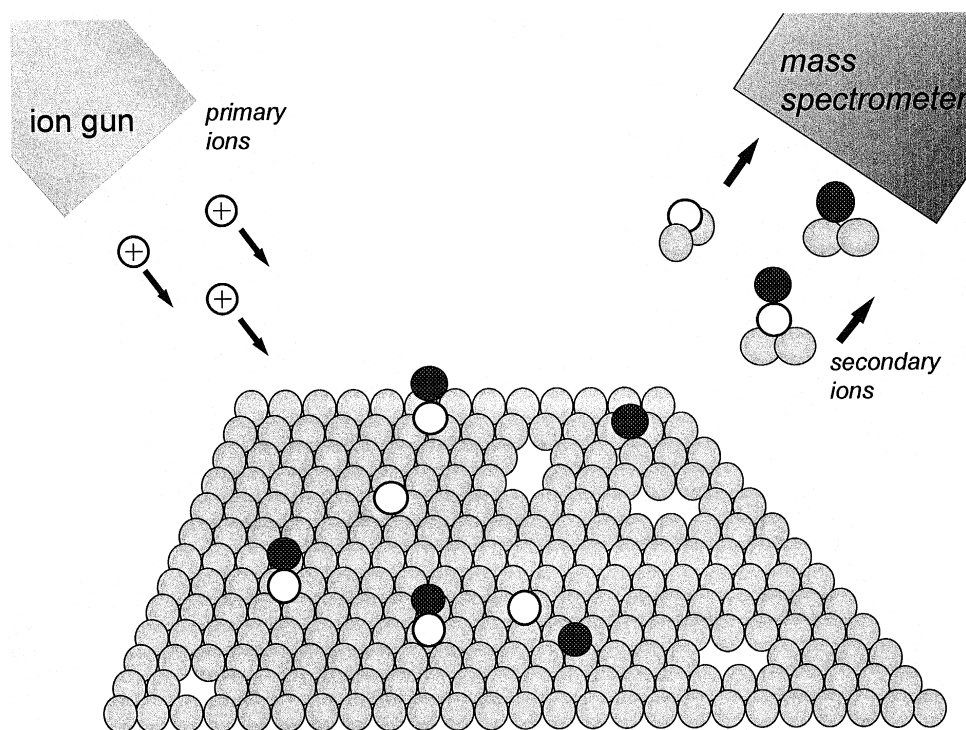


Fig. 1. Secondary ion emission from a metal surface covered by a diatomic molecule such as NO and its atomic dissociation products N and O.

secondary ion yields of one element can vary tremendously with its chemical environment. This matrix effect and the elemental sensitivity variation of five orders of magnitude across the periodic table make quantitative interpretation of SIMS spectra of, e.g., technical catalysts, extremely difficult. In working with adsorbates on metal single crystals, matrix effects are easier to identify and to understand, such that quantitative analysis of SIMS intensities is often possible.

SIMS is strictly speaking a destructive technique, but not necessarily a damaging one. In the dynamic mode, used for making concentration depth profiles, several tens of monolayers (ML) are removed per minute. In static SIMS, however, the rate of removal corresponds to 1 ML per several hours, implying that the surface structure does not change significantly during the measurement (between seconds and minutes). In this case, one can be sure that the molecular ion fragments are truly indicative of the chemical structure on the surface. Static SIMS is a very gentle, non-damaging technique, which causes less damage to a surface than for example Auger spectroscopy or even standard XPS do. It is this static mode of SIMS which is used to monitor the changes in concentrations of adsorbed species that accompany surface reactions.

Fig. 1 represents a metal surface covered by diatomic molecules such as CO or NO and their atomic dissociation products, C or N, and O. Among the secondary ions are clusters of the type MCO^+ , M_2CO^+ , M_2C^+ and M_2O^+ (M = metal) which are characteristic of adsorbed CO, C and O, respectively. Very often, intensity ratios of the type MCO^+/M^+ , M_2CO^+/M_2^+ , M_2C^+/M_2^+ and M_2O^+/M_2^+ have been found to correlate well with the respective adsorbate coverages. The validity of such correlations has been extensively checked in adsorption systems such as CO on palladium [5], H_2 on nickel [6] and NO on rhodium [7,8].

While this approach has been outstandingly successful for adsorption of simple gases (CO,

NO, H_2 , C_2H_4) on first and second row transition and group Ib metals, it does not work for third row metals as platinum. The relatively high ionization potential of these metals significantly lowers the probability of secondary ion formation, while in addition the detection efficiency for these relatively high mass clusters is substantially lower as well.

3. Applications of static SIMS in catalytic surface chemistry

Several types of SIMS experiments have appeared useful in surface chemistry:

- characterization of adsorbed species,
- kinetics of elementary dissociation or association reactions on the surface in temperature programmed SIMS experiments,
- identification of rate determining steps by revealing the majority intermediates on the surface during a catalytic reaction, and
- unravelling of complex reaction pathways.

It has often proved useful to combine SIMS, monitoring reacting species on the surface, with temperature programmed desorption (TPD) (or TPRS) to follow the evolution of products. We discuss examples of such experiments in the following.

3.1. Adsorption of NO on Rh (111)

The SIMS spectra of Fig. 2 illustrate molecular and dissociative chemisorption of NO on rhodium (111). The lower spectrum represents the region between 200 and 250 amu of 0.12 ML of NO on Rh (111) adsorbed at 100 K, where the NO bond is not expected to break. The spectrum shows characteristic ions of Rh_2^+ (206 amu), Rh_2H^+ (207 amu), and Rh_2NO^+ (236 amu), in accordance with molecularly adsorbed NO and some contamination by hydrogen from the background. The small signals at masses 220 and 222 are due to Rh_2N^+ and Rh_2O^+ , and are attributed to fragmentation of the Rh_2NO^+ parent species. If the surface is

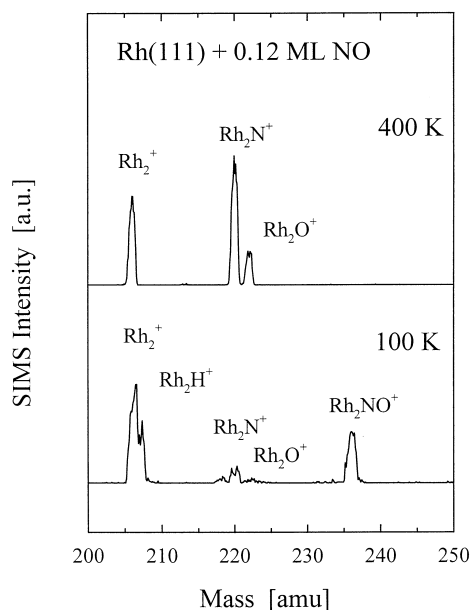


Fig. 2. SIMS spectra of the Rh (111) surface after adsorption of 0.12 ML NO at 100 K (lower spectrum), illustrating molecular adsorption, and after subsequent heating to 400 K (upper spectrum), illustrating dissociation into N and O.

heated to 400 K, NO is known to dissociate while excess NO (and impurity hydrogen) desorbs [7]. The upper SIMS spectrum of Fig. 2 confirms indeed that all NO has disappeared and that instead the surface contains N and

O-atoms, as indicated by the Rh_2N^+ and Rh_2O^+ secondary ions, respectively. Hence, static SIMS readily identifies molecular NO as well as its dissociation products N and O on the rhodium surface.

In the dynamic experiments of Fig. 3, static SIMS reveals how the rhodium surface fills up with NO and its dissociation products during exposure to a constant pressure of $2 \cdot 10^{-8}$ mbar of NO at a fixed temperature. As above, the intensity ratios $\text{Rh}_2\text{NO}^+/\text{Rh}_2^+$, $\text{Rh}_2\text{N}^+/\text{Rh}_2^+$, and $\text{Rh}_2\text{O}^+/\text{Rh}_2^+$ are used to reflect at least semiquantitatively the coverages of NO, N and O.

At 150 K, NO adsorbs exclusively molecularly as is illustrated by the left panel of Fig. 3. The non-zero intensities of the $\text{Rh}_2\text{N}^+/\text{Rh}_2^+$, and $\text{Rh}_2\text{O}^+/\text{Rh}_2^+$ SIMS intensity ratios are attributed to fragmentation of the Rh_2NO^+ cluster ion. Partial dissociation occurs at 300 K. As Fig. 3 shows, the $\text{Rh}_2\text{N}^+/\text{Rh}_2^+$, and $\text{Rh}_2\text{O}^+/\text{Rh}_2^+$ SIMS intensity ratios rise well before the $\text{Rh}_2\text{NO}^+/\text{Rh}_2^+$ ratio does, indicating that initially NO dissociates instantaneously upon adsorption. However, as the surface fills up with N and O atoms, dissociation is retarded, because the necessary ensembles for dissociation (which we discuss later on), are no longer

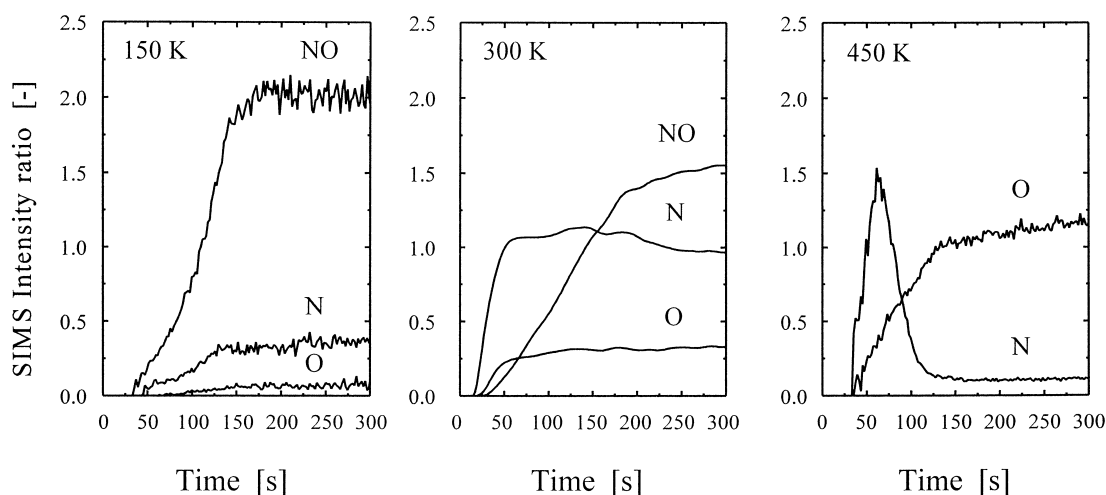


Fig. 3. Development of the $\text{Rh}_2\text{NO}^+/\text{Rh}_2^+$, $\text{Rh}_2\text{N}^+/\text{Rh}_2^+$, and $\text{Rh}_2\text{O}^+/\text{Rh}_2^+$ SIMS intensity ratios (indicated by NO, N and O, respectively) as a function of time when a Rh (111) crystal is exposed to 2.10^{-8} mbar NO at 150, 300 and 450 K.

available. Hence, the empty sites become occupied by molecular NO.

A different picture arises at temperatures above the desorption temperature of molecular NO, which is around 430 K. At 450 K, dissociation is so fast that molecular NO can not be observed on the surface. Initially, both atomic nitrogen and oxygen build up on the surface, as indicated by the simultaneous increase of the $\text{Rh}_2\text{N}^+/\text{Rh}_2^+$, and $\text{Rh}_2\text{O}^+/\text{Rh}_2^+$ SIMS intensity ratios. However, after some time (about 65 s in Fig. 3) the $\text{Rh}_2\text{N}^+/\text{Rh}_2^+$ SIMS intensity ratio starts to decrease, indicating that N_2 desorbs. Being a second-order reaction, the rate of N_2 desorption increases with coverage as θ_{N}^2 , while repulsive interactions with atomic oxygen enhance the rate even further. The decrease in the atomic nitrogen-coverage is accompanied by an increase of the atomic oxygen-coverage. Note that the O-signal continues to increase at the same rate as initially on the empty surface, implying that the NO-dissociation rate remains constant. Despite the fact that the N-production rate (equal to the NO-dissociation rate) remains constant, the N-coverage decreases. This implies that the N_2 desorption rate is accelerated

with increasing O-coverage. After approximately 125 s, the $\text{Rh}_2\text{N}^+/\text{Rh}_2^+$ intensity ratio becomes constant, and the dissociation rate decreases, indicative for a steady state situation with respect to N-atoms, which may endure until the surface becomes fully saturated. Evidence has been found that some of the nitrogen, and perhaps some of the oxygen as well, goes into subsurface positions [9].

3.2. Dissociation kinetics of NO on rhodium (111)

The usefulness of combining TPD, which detects products desorbing from the surface, and a technique that reveals reactions on the surface such as SIMS, is demonstrated by Fig. 4 [7]. NO is adsorbed on Rh (111) at 100 K, and subsequently heated at a rate of 10 K s^{-1} while the mass spectrometer detects desorbing N_2 and NO in TPD mode and secondary ions characteristic for NO and N-atoms in SIMS mode. If the initial coverage of adsorbed NO is low, 0.15 ML in Fig. 4, all NO is seen to dissociate around room temperature, as reflected by the disappearing $\text{RhNO}^+/\text{Rh}^+$ signal and the ap-

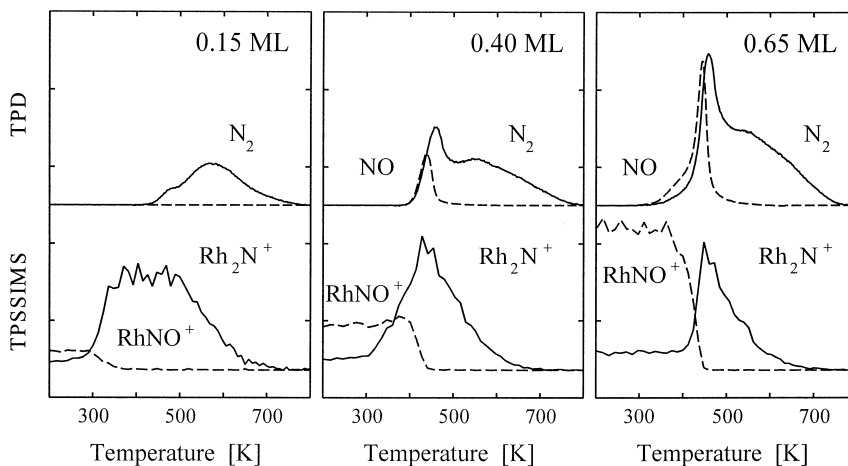


Fig. 4. The NO (dashed line) and N_2 (full) TPD rates (top), and $\text{Rh}_n\text{NO}^+/\text{Rh}$ (dashed) and $\text{Rh}_2\text{N}^+/\text{Rh}$ (full) TPSSIMS ion intensity ratios (bottom), during temperature programmed reaction of NO on Rh (111), for low (left panel), medium (central panel) and high (right panel) initial NO coverages. The NO TPD spectra have been divided by a factor of 4 with respect to the N_2 TPD spectra. The adsorption temperature was 100 K; the heating rate was 10 K s^{-1} .

pearing $\text{Rh}_2\text{N}^+/\text{Rh}_2^+$ signal. The N-atoms recombine to desorb as N_2 between 500 and 700 K as indicated directly by the N_2 TPD signal and also by the decreasing Rh_2N^+ intensity in SIMS (the small shoulder on the low temperature side of the N_2 TPD curve is due to desorption of impurity CO).

Repeating the experiment with a surface saturated with NO (0.65 ML; right panel of Fig. 4), gives an entirely different picture. The first thing that happens during heating is the desorption of NO around 430 K, followed almost instantaneously by dissociation of NO, evidenced by the rising Rh_2N^+ intensity, and desorption of N_2 . The interpretation is that NO-dissociation is a ‘demanding’ reaction which needs an ensemble of several empty sites. Such ensembles are abundantly present at low initial NO-coverages, but not at all when the surface is saturated with NO. Indeed, an experiment with an intermediate NO-coverage of 0.40 ML (middle panel of Fig. 4) shows that NO-dissociation starts at 300 K but continues to occur through over 400 K after some of the NO has desorbed.

Assuming that, at least for low coverages, the ratios $\text{RhNO}^+/\text{Rh}^+$ and $\text{Rh}_2\text{N}^+/\text{Rh}_2^+$ are proportional to the coverages of NO and N, θ_{NO} and θ_{N} , we can fit the curves with the following kinetic expression:

$$-\frac{d\theta_{\text{NO}}}{dt} \equiv \frac{d\theta_{\text{NO}}}{dt} \equiv \nu\theta_{\text{NO}}(\theta)^n e^{-E_{\text{dis}}/RT}$$

yielding and activation energy of dissociation of 65 ± 6 kJ mol⁻¹, a preexponential factor of $10^{11 \pm 1}$ s⁻¹ and between three and four adsorption sites per ensemble of rhodium atoms needed for dissociation [7]. The latter ensemble size is in good agreement with theoretical predictions of de Koster and van Santen [10]. Desorption of NO and N_2 occurs with first- and second-order rate parameters as listed in Table 1.

3.3. Reactions of NO with hydrocarbons on rhodium

Reactions between NO and hydrocarbons have received far less attention than reduction

Table 1

Kinetic parameters of several elementary surface reactions on Rh (111)

Reaction	E_{act} (kJ mol ⁻¹)	ν (s ⁻¹)	Reference
$\text{NO}_{\text{ads}} + * \rightarrow \text{N}_{\text{ads}} + \text{O}_{\text{ads}}$	65 ± 6	$10^{11 \pm 1}$	[7]
$\text{NO}_{\text{ads}} \rightarrow \text{NO}_{\text{g}} + *$	113 ± 10	$10^{13.5 \pm 1}$	[7]
$\text{C}_{\text{ads}} + \text{N}_{\text{ads}} \rightarrow \text{CN}_{\text{ads}}^*$	111 ± 11	$10^{11 \pm 1}$	[11]
$\text{CN}_{\text{ads}}^* \rightarrow \text{C}_{\text{ads}} + \text{N}_{\text{ads}}$	210 ± 15	$10^{13 \pm 1}$	[11]
$\text{N}_{\text{ads}} + \text{N}_{\text{ads}} \rightarrow \text{N}_2 + 2*$	118 ± 10	$10^{10 \pm 1}$	[7,9]
$\text{NH}_{2,\text{ads}} + \text{H}_{\text{ads}} \rightarrow \text{NH}_{3,\text{ads}} + *$	69 ± 6	—	[12]
$\text{NH}_{3,\text{ads}} \rightarrow \text{NH}_{3,\text{g}} + *$	81 ± 5	$10^{13 \pm 1}$	[13]

of NO by CO or by H_2 , yet such reactions are relevant for obtaining a complete picture of the complicated surface chemistry of a practical three-way catalyst. Among the most abundant hydrocarbons in automotive exhaust gas are methane, acetylene, ethylene, propylene, benzene and toluene [14]. The more reactive hydrocarbons assist in the reduction of NO by removing O-atoms from the surface. We will first briefly describe how ethylene decomposes on rhodium, and then discuss the reaction of ethylene coadsorbed with NO.

The decomposition of small olefins such as ethylene and propylene on noble metals such as platinum and rhodium has been studied extensively [15–22]. On rhodium, ethylene adsorbs molecularly below about 140 K, which is reflected by a characteristic RhC_2H_4^+ signal in SIMS [15]. The ethylene starts to convert to an intermediate which most likely is vinyl, $\text{CH}=\text{CH}_2$ at 140 K [15], while at about 180 K it reacts to ethylidyne, CCH_3 , and a H-atom. The ethylidyne is recognized in SIMS by its intense secondary CH_3^+ ion. Around 300 K, the ethylidyne starts to decompose to acetylide, CCH , and CH , and eventually, carbidic carbon, while hydrogen desorbs in decomposition-limited steps [23]. The saturation coverage of ethylidyne on Rh (111) is 0.25 ML, while that of ethylene is 0.33 ML. Most of the excess ethylene is seen to desorb at about 200 K when the surface reaction to ethylidyne occurs.

The TPD/TPSIMS experiment of Fig. 5 illustrates the reactions that occur when 0.20 ML

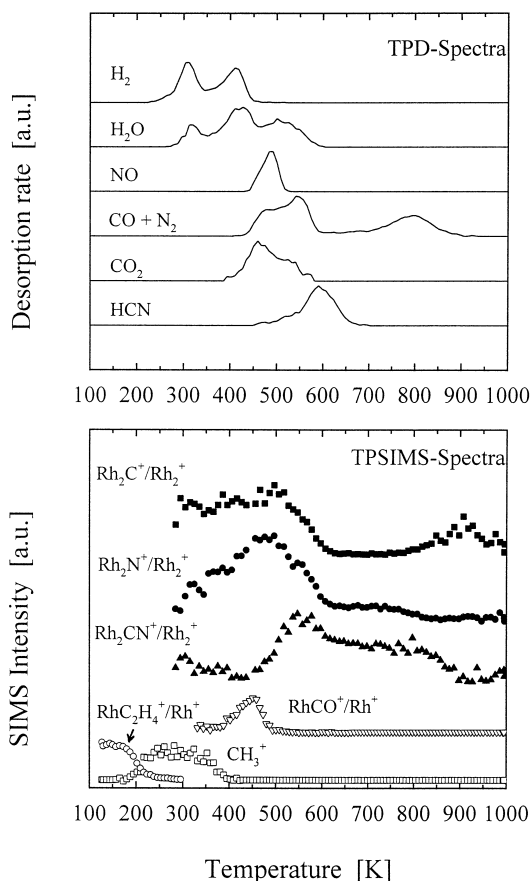


Fig. 5. Temperature programmed reactions of 0.12 ML of ethylene coadsorbed with 0.20 ML of NO as followed by TPD and SIMS (see text for explanation). The adsorption was done at 100 K, and the heating rate was 10 K s^{-1} .

of NO is coadsorbed with 0.12 ML of ethylene on Rh (111) [24]. The desorption traces in the upper half of the figure indicate that NO and C_2H_4 not only react to the products that are desirable in automotive exhaust catalysis, N_2 , CO_2 and H_2O . Significant amounts of H_2 , CO, NO and even HCN desorb as well. The signal at mass 28 may reflect up to three products (C_2H_4 , N_2 and CO). Careful monitoring of the cracking patterns confirms that the two peaks around 500 K are due to CO while that above 700 K is caused by N_2 .

The static SIMS signals in the lower half of Fig. 5 give a detailed picture of processes on the surface. Discussing the curves from low to high

temperature, the first reaction revealed by SIMS is the conversion of adsorbed ethylene, visible by the RhC_2H_4^+ cluster ion, to ethylidyne, reflected by CH_3^+ , between 180–200 K. The next step is the dissociation of adsorbed NO, starting at about 280 K and revealed by the steeply rising Rh_2N^+ intensity. This implies that from 280 K on there are N- and O-atoms on the surface. H-atoms are available from the ethylene to ethylidyne formation, and indeed, water desorption is seen to start at 280 K, the moment that NO starts to dissociate. A mass 30 desorption peak at 480 K indicates that not all NO dissociates. Carbon becomes available when ethylidyne decomposes, between 350 and 400 K. Here CO starts to form on the surface (reflected by the RhCO^+ ion), followed instantaneously by the desorption of CO_2 , and CO at slightly higher temperatures.

At 500 K and higher the signals characteristic of adsorbed nitrogen and carbon atoms start to decrease, while at the same time CN species build up on the surface as reflected by the Rh_2CN^+ ion, while the TPD spectra reveal desorption of HCN. In the absence of surface hydrogen, these CN species remain stable up to about 750 K, where N_2 is detected in the gas phase. Note that CN formation retards the desorption of N_2 to temperatures that are up to 200 K higher than observed when N is the only adsorbate present. The last reaction revealed by Fig. 5 is the dissolution of surface carbon into the rhodium just above 900 K.

The experiment of Fig. 5 illustrates very well how static SIMS complements the information on product formation in TPD by providing qualitative but fairly detailed evidence for reactions occurring on the surface. Obtaining kinetic parameters from such a complicated reaction mechanism is not warranted, but one can study several steps in the $\text{NO} + \text{C}_2\text{H}_4$ reaction in isolation. Actually, the NO-dissociation study of Fig. 4, and the C_2H_4 decomposition study reported in Ref. [15] are two examples and the recombination reaction between adsorbed C and N-atoms discussed in Section 3.4 is another.

3.4. Kinetics of the reaction $C_{ads} + N_{ads} \rightarrow CN_{ads}$

In order to study this reaction, one needs to be able to prepare surfaces covered by C and N-atoms only. Decomposition of ethylene, provided at low coverages, produces C-atoms below the onset of CN formation at 480 K [15]. A rhodium surface covered by N-atoms only, is readily prepared by decomposition of NO at 400 K followed by hydrogenation of the O-atoms at the same temperature. If one starts with NO-coverages below 0.20 ML, where all the NO dissociates [7], the eventual coverage of N-atoms equals that of the initially molecular NO [12].

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 is not observed [11]. A temperature programmed SIMS experiment was done to monitor the coverages of carbon, nitrogen and CN

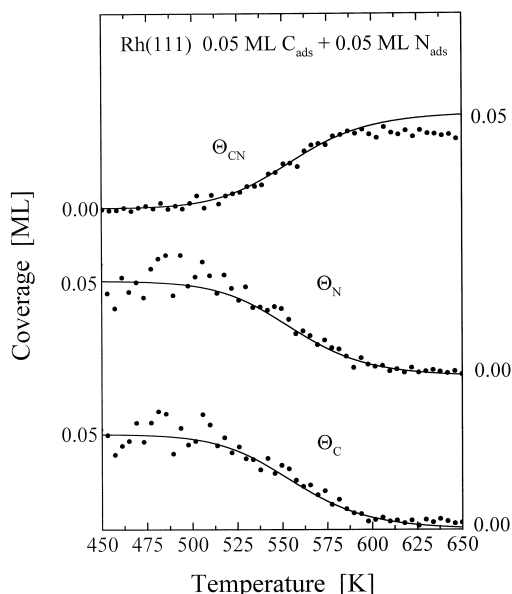


Fig. 6. Change of the surface coverages of C, N and CN vs. temperature as derived from the SIMS Rh_2C^+/Rh_2^+ , Rh_2N^+/Rh_2^+ and Rh_2CN^+/Rh_2^+ intensity ratios, respectively. The initial N and C coverages were 0.05 ML each and the heating rate was 4 K s^{-1} . The solid lines represent fits with $\nu = 10^{11} \text{ s}^{-1}$ and $E_{act} = 111 \text{ kJ mol}^{-1}$.

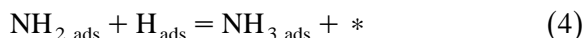
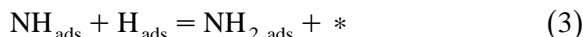
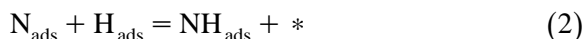
species through the Rh_2C^+ , Rh_2N^+ and Rh_2CN^+ secondary cluster ions. As Fig. 6 shows, a reaction between C-atoms and N-atoms to adsorbed CN species starts at 500 K and is completed at about 625 K. The data can satisfactorily be fitted with the following rate equation:

$$-\frac{d\theta_C}{dt} = \frac{d\theta_{CN}}{dt} = \nu e^{-E_{act}/RT} \theta_C \theta_N$$

yielding $E_{act} = 111 \pm 10 \text{ kJ mol}^{-1}$ and $\nu = 10^{11 \pm 1} \text{ s}^{-1}$, suggesting that this reaction is indeed an elementary one [25].

3.5. Hydrogenation of N_{ads}

As in the NO + ethylene reaction N-atoms are present together with H-atoms on the surface, one should also consider hydrogenation of nitrogen to ammonia as a possible reaction pathway. We have studied this reaction separately by starting with a Rh (111) surface and a certain coverage θ_N and exposing it to a background pressure of H_2 . The following sequence of elementary steps is then expected.



The rate of ammonia formation is too small to be measured directly with acceptable precision by a mass spectrometer, but the rate of reaction can accurately be determined by measuring the decrease in the coverage of N_{ads} , by means of thermal desorption after hydrogenation. The question now is which of the steps in the scheme determines the rate.

Ammonia formation was found to be first order in both the N-atom coverage and the partial pressure of hydrogen [12]. The latter implies that reaction (2) in the scheme above, does not determine the rate. Hence, either reaction (3), (4) or (5) should be considered rate determining.

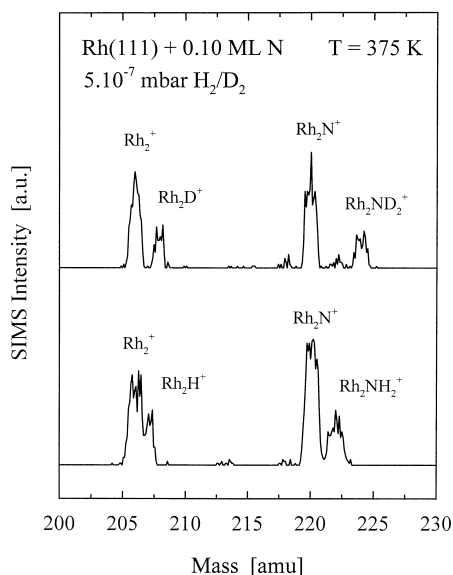


Fig. 7. SIMS spectra of the Rh (111) surface during a hydrogenation experiment showing the presence of H (Rh_2H^+ : 207 amu), N (Rh_2N^+ : 220 amu), NH_2 (Rh_2NH_2^+ : 222 amu) as reaction intermediates. Peak assignments were verified by using D_2 instead of H_2 . The spectrum was taken after 20 s of reaction, the H_2 and D_2 pressures were 5.10^{-7} mbar and $T = 375$ K. The initial N coverage was 0.10 ML.

In order to identify a rate determining step, one needs to establish which species reside on the surface during hydrogenation. The SIMS spectrum in Fig. 7, measured during hydrogenation at 375 K shows peaks of Rh_2^+ , Rh_2H^+ , Rh_2N^+ , and Rh_2NH_2^+ . SIMS measurements of the N-hydrogenation by means of deuterium give better mass separation and confirm the assignments. The fact that the Rh (111) surface contains a significant concentration of NH_2 species during the hydrogenation of N_{ads} clearly points to the reaction between $\text{NH}_{2,\text{ads}}$ and H_{ads} , step (4) in the scheme above, as the rate-determining step.

Finally, measuring the temperature dependence of the rate yields an effective activation energy of 33 kJ mol^{-1} (erroneously reported as 40 kJ mol^{-1} in a previous publication [12]) and a preexponential factor of 10^2 s^{-1} . If we write the rate of reaction as

$$r = k_4 \theta_{\text{NH}_2} \theta_{\text{H}} \approx k_4 K_{\text{H}_2}^{1/2} \theta_{\text{NH}_2} p_{\text{H}_2}^{1/2}$$

while the heat of adsorption of H_2 equals 72 kJ mol^{-1} , the true activation energy of the rate determining step (4) becomes 69 kJ mol^{-1} (note that we erroneously reported a value 76 kJ mol^{-1} in Ref. [12]).

4. Concluding remarks

Several successful SIMS studies have now been reported in the field of surface chemistry. A recent review [4] lists about 70 applications dealing with adsorption and reaction of gases on transition metal surfaces. Among these are thermal decomposition reactions of hydrocarbons and oxygenated species such as methanol and ketene, hydrogenation of CO, surface carbon and thiophene, oxidation of CO and methanol, H–D exchange in hydrocarbon species, to mention just a few highlights. Due to the complicated and only partially understood mechanism of secondary ion formation, applications of SIMS requiring (semi)quantitative interpretations are limited to studies on metal surfaces. On metals, the matrix effect is reasonably well described as the variation in work function due to the presence of adsorbates [2,4]. Hence, in practice, intensity ratios of the type $\text{RhNO}^+/\text{Rh}^+$ correlate sufficiently well with the coverage of the adsorbate, that changes in the ratios can be taken as relative changes in surface concentration. This is sufficient for permitting meaningful kinetic analysis.

The examples discussed in this paper illustrate that static SIMS together with TPD/TPRS forms a highly useful combination to study reactions on surfaces. SIMS, applied in temperature programmed or constant temperature mode, monitors processes that occur on the surface, while TPD or TPRS detects the evolution of products. The example on surface reactions of coadsorbed NO and ethylene, Fig. 5, nicely illustrates the wealth of information one obtains on this complex reaction mechanism.

For catalysis, the option to study elementary surface reactions and obtain corresponding ele-

mentary kinetic parameters is particularly attractive, for two reasons. First, all catalytic reaction mechanisms consist by necessity of several elementary steps, and in order to model the overall kinetics of the process, all information on the constituent reaction steps is highly welcome. Second, elementary kinetic parameters and equilibrium constants form the link between molecular properties and reactivity, as described by statistical thermodynamics and, e.g., transition state theory [25]. Ground state properties of adsorbed species are accessible by spectroscopy, but in general transition states are not. If the preexponential factor and activation energy of the surface reaction are known, one can derive important additional information on the transition state of the reaction step.

In this respect, we note that the 'Grand Data Base of Surface Science' contains a multitude of well documented data on adsorbed species, their adsorption energies and their ordering behavior, and a reasonable number of catalytic reaction rates expressed as turnover frequencies, but, unfortunately, preciously little on the kinetics of elementary reactions on the surface. We hope to have illustrated that SIMS/TPD studies may contribute substantially by providing data as collected in Table 1.

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