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NO dissociation on rhodium

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The desorption and dissociation of nitric oxide on a polycrystalline Rh foil were studied by means of combined temperature-programmed desorption (TPD) and static secondary ion mass spectrometry (SSIMS). The latter method was employed either under isothermal conditions or in a temperature-programmed mode (TPSSIMS). After carefully calibrating the secondary ion intensities by means of TPD, the NO dissociation kinetics were quantitatively evaluated for low NO coverages. Fitting the SSIMS data with a Polanyi–Wigner ansatz and assuming first-order kinetics, we found an activation energy, $E = 8 \pm 2\,\mathrm{kJ/mol}$, and a preexponential, $\nu = 10^{-0.2\pm0.4}\,\mathrm{s}^{-1}$. The data were confirmed by independent isothermal SSIMS measurements at several temperatures between 80 and 330 K. The fairly unusual rate parameters are discussed in relation to similar results obtained recently from measurements on Rh single crystal surfaces.

Keywords: nitric oxide; rhodium; dissociation kinetics; static secondary ion mass spectrometry; temperature-programmed desorption

1. Introduction

One of the important reactions in air pollution control is the catalytic reduction of nitric oxide. The decomposition into oxygen and nitrogen atoms is considered to be a key step preceding any further reaction with CO, H_2 or other agents. Quite remarkably, only a limited number of studies have been devoted to determining the detailed kinetics of NO decomposition over rhodium [1–8] which is the most effective metal in three-way catalysts. Quantitative EELS (electron energy loss spectroscopy) measurements on atomically dense Rh single crystal planes revealed rate parameters with a range of values usually considered "normal" for the decomposition of diatomic molecules on metallic surfaces. For example, on Rh{111} an activation energy, $E = 80\,\mathrm{kJ/mol}$, was determined along with a preexponential,

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$\nu = 10^{14}\,\mathrm{s}^{-1}$ [1]. Similar values were found for measurements on Rh{100}: $E = 44\,\mathrm{kJ/mol}$ and $\nu = 10^{12}\,\mathrm{s}^{-1}$ [3]. Recently, however, "abnormal" decomposition kinetics were seen to dominate the strongly corrugated Rh{110} plane: using calibrated temperature-programmed static secondary ion mass spectrometry (TPSSIMS), Schmatloch et al. [6] determined an activation energy of $E = 15 \pm 2\,\mathrm{kJ/mol}$ and a preexponential of $\nu = 10^{1.9\pm0.5}\,\mathrm{s}^{-1}$. These values were confirmed in a subsequent study by Comelli et al. [7] employing Auger line shape analysis.

At present, no consistent explanation can be given for the "slow" decomposition kinetics of NO on Rh{110}. It has been assumed that a Rh atom displacement is coupled to N–O bond breaking, so that the "true" kinetics would probably not be revealed by fitting the data to a Polanyi–Wigner equation [6].

In view of the above results one is led to conclude that NO decomposition on Rh is structure sensitive. According to a very recent study on Rh{111} by Borg et al. [8], the influence of the surface structure is possibly not as strong as hitherto believed. Based on an experimental approach similar to ours the authors found that $E = 40 \pm 6\,\mathrm{kJ/mol}$ and $\nu = 10^{6\pm1}\,\mathrm{s}^{-1}$. These values are also quite low though different from those obtained for Rh{110}. Borg et al. [8] considered an ensemble of several Rh atoms to be necessary for NO decomposition so that their rate parameters would have to be corrected upwards.

The present investigation will demonstrate the kinetic behavior on a polycrystalline Rh foil. On the one hand, the presence of a large number of step sites in the surface of such a sample bears similarities with the corrugated Rh{110} plane. On the other hand, reconstructive phenomena are less likely to occur due to the dominating presence of stable, low-index planes. Thus, using overall low NO coverages, the intrinsic activity of step sites may be probed for diffusion-mediated decomposition.

The NO reaction with polycrystalline Rh surfaces has already been investigated by other researchers [9–12], but the detailed NO dissociation kinetics were not addressed. Apart from an obvious interest in structural effects, current investigations in our laboratory are also concerned with a kinetic modelling of the CO/NO and D_2/NO reactions on Rh. Both reactions were found to exhibit periodic oscillations in the temperature range around 900 K on Rh{110} [13–15].

2. Experimental

2.1. GENERAL

Experiments were performed in a multimethod UHV analysis chamber which was described in detail elsewhere [16]. The base pressure was less than 10^{-10} mbar. The SIMS spectra were taken by scanning a 5 keV Ar^{+} beam across the surface of the sample. Static conditions were ensured by limiting the current density to a few $\mathrm{nA/cm}^{2}$. Low temperature measurements with constant coverage and variable primary ion current densities confirmed the static operation in SIMS. Heating rates in TPSSIMS and TPD were 0.5 K/s and 5 K/s respectively.

The rhodium foil (Johnson Matthey, 99.9%, 25 μm thickness) was mounted on the head of a sample rod by using two spotwelded tantalum strips which allowed linear heating up to more than 1300 K and cooling with liquid nitrogen to 80 K. Temperatures were measured by a chromel–alumel thermocouple spotwelded to the rear of the foil.

The surface was cleaned by subsequent cycles of argon ion sputtering at 800–1000 K, heating at an oxygen pressure of 10^{-6} mbar at 900 K and flashing to 1300 K. Argon ion sputtering removed contaminations of sulphur and phosphorus; heating in oxygen was used to remove carbon from the surface. These cycles were repeated for several weeks until no contaminations were detectable with either AES or SSIMS. Nitric oxide (Messer Griesheim 99.8%) was used without further purification. Gases were dosed at 80–100 K.

2.2. PROCEDURES AND CALIBRATION

A proper calibration of the SSIMS intensities forms the basis for a quantitative evaluation of the rate parameters from real-time SSIMS measurements. Brown and Vickerman [17], in a study of CO adsorption on Pd single crystal surfaces, found that the surface coverage is proportional to the sum of cluster ion ratios:

$$\Theta_X \approx \sum_i \frac{\mathrm{Me}_i\mathrm{X}^+}{\mathrm{Me}_i^+} \tag{1}$$

(X being the adsorbate under investigation). This relation was confirmed for several systems in our laboratory [6,18]. In this investigation, both ratios $\mathrm{Rh_1NO^+/Rh_2^+}$ and $\mathrm{Rh_2NO^+/Rh_2^+}$ revealed an identical dependence on the coverage up to at least $\Theta = 0.5$ ML. The ratio $\mathrm{Rh_2NO^+/Rh_2^+}$ was usually higher by a factor of about 3–4 but more affected by noise. Contributions of $i = 3$ or higher were negligible. Therefore we restricted our TPSSIMS measurements on low $\mathrm{NO_{ad}}$ coverages and on clusters with $i = 1$ which exhibit better signal-to-noise ratios. Quite similarly, the case $i = 1$ was considered representative in studies of NO on Rh{110} [5,6] and on Rh{111} [8].

The TPSSIMS relative intensities were evaluated by calculating the derivatives $-\mathrm{d}\theta_{\mathrm{NO}}/\mathrm{d}t = -\beta^{-1}\mathrm{d}\theta_{\mathrm{NO}}/\mathrm{d}T$ (with β being the heating rate) in order to obtain the rate of desorption or dissociation of the adsorbed NO.

3. Results

3.1. GENERAL

Fig. 1 presents results of a calibration measurement in which the SSIMS cluster ion ratios were compared with the TPD areas evaluated by integrating under the N_2

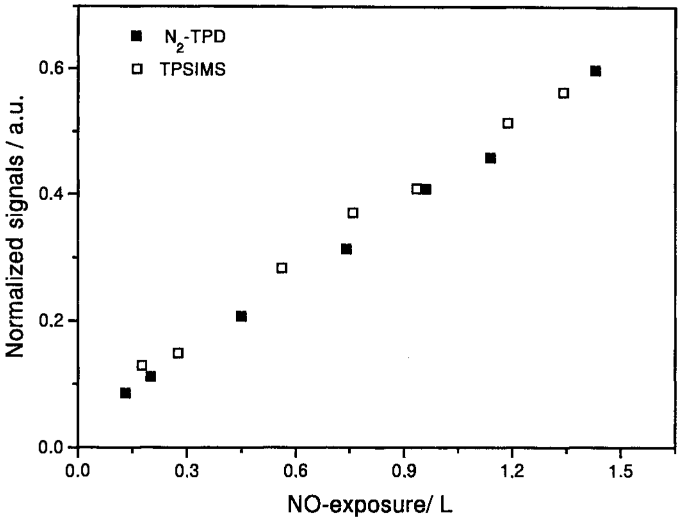

Fig. 1. Normalized $Rh_1NO_1^+/Rh_1^+$ TPSSIMS cluster intensities and N_2-TPD peak areas plotted for NO exposures up to 1.5 L, showing the linear relationship between TPD and TPSSIMS signals ($1\,L = 1.3 \times 10^{-6}$ mbar s).

peaks after various initial exposures. For the low coverages used, NO_{ad} dissociates completely and, therefore, O_2 and N_2 are the only species desorbing from the surface. Thus, both can be taken as a direct measure of the amounts of dissociating NO_{ad} species. Using the O_2 desorption signal for calibration might cause problems at very low coverages, because small amounts of oxygen may always react with hydrogen or CO, both of which are major components of the residual gas in a stainless steel vacuum system. In addition, thermal O_2 desorption occurs at rather high temperatures (up to 1300 K) which are difficult to handle. Thus N_2-TPD was used for calibrating the SSIMS intensity ratios.

According to fig. 1, a linear relationship between TPD and TPSSIMS is found for exposures and coverages up to 1.4 L (1 L (langmuir) $= 1.3 \times 10^{-6}$ mbar s) or $\Theta = 0.5$ ML respectively. This behavior can be explained in terms of precursor adsorption kinetics and is similar to observations of NO on Rh{110} [6] or Rh{111} [8].

3.2. TEMPERATURE-PROGRAMMED EXPERIMENTS

In fig. 2, TPD and TPSSIMS spectra are shown for three different coverages in the temperature range between 100 and 750 K. For the objective of this paper the upper panel (a) (~ 0.2 ML NO at 110 K) is most important. It is seen that N_2 undergoes thermal desorption at a peak temperature of $T_2 = 600$ K. On the other hand, TPSSIMS reveals a single peak at $T_1 = 252$ K under similar experimental conditions. Thus, we are led to conclude that NO_{ad} undergoes complete dissociation

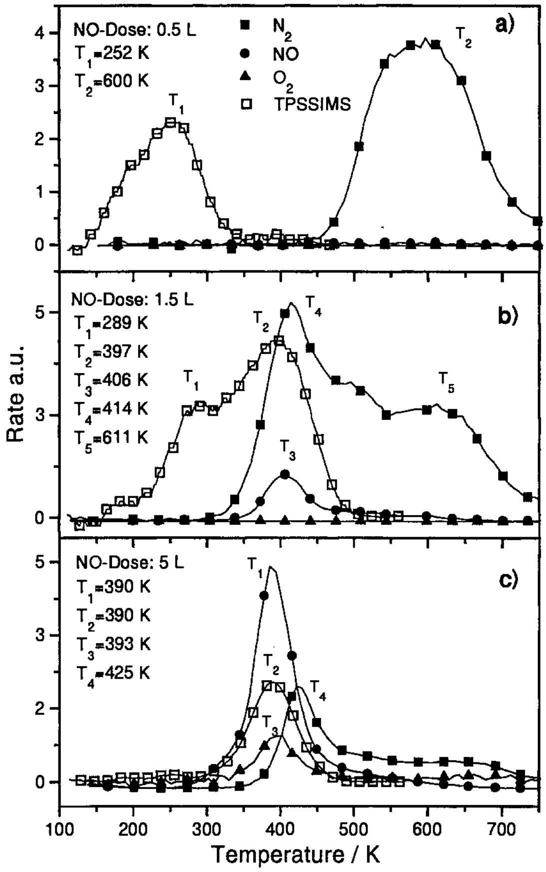

Fig. 2. TPSSIMS and TPD data plotted for three different NO coverages. (a) Exposure of 0.5 L, showing that only dissociation occurs below 400 K (no NO-TPD signal), (b) intermediate exposure of 1.5 L, so that NO desorption becomes likewise detectable, (c) high exposure of 5 L, for which NO thermal desorption is predominating over dissociation due to site blocking effects in the adsorbed layer (O_2-TPD multiplied by a factor of 10). (■) N_2, (●) NO, (▲) O_2, (□) TPSSIMS.

heating the surface. Moreover, it is clear that TPSSIMS can be used in studies of the NO dissociation kinetics for the limit of low coverages.

Part (b) of fig. 2 shows the situation for an intermediate coverage of ~0.5 ML. The TPSSIMS and TPD signals have changed position and shape if compared to panel (a). NO thermal desorption is now observable with a peak maximum at $T_3 = 406\,\mathrm{K}$. In addition, another N_2 feature appears around $T_4 = 414\,\mathrm{K}$. The TPSSIMS signal consists of two peaks at $T_1 = 289\,\mathrm{K}$ and $T_2 = 397\,\mathrm{K}$, respectively, which are, however, not completely resolved. The smaller peak at lower temperature can again be attributed to dissociation, since thermal desorption does not occur in this temperature regime. Above 300 K dissociation and desorption are most likely to proceed simultaneously. The situation is rather complicated because there are several processes influencing each other. Dissociation can still start at low temperatures because a certain number of vacant sites is available even at a coverage of ~ 0.5 ML. The rate, however, is lower than in panel (a). As soon as thermal desorption is activated, additional vacancies become available so that the dissociation process accelerates. Consequently, increasing amounts of surface nitrogen atoms cause increasing N_2 thermal desorption. The occurrence of an N_2-TPD peak maximum at much lower temperatures than in panel (a) may be explained by the larger nitrogen coverage and by assuming the existence of repulsive interactions within the adsorbed layer. It is most likely that adsorbed oxygen atoms further destabilize the nitrogen adsorbate [8,19].

The lower panel (c) of fig. 2 shows results which were obtained for a nearly saturated surface. The TPSSIMS data indicate that dissociation at low temperatures ($T < 270$ K) is insignificant. The positions of the respective – very small – peaks, however, are in good agreement with those at lower initial coverages, see panels (a) and (b). The major TPSSIMS peak coincides with the respective TPD peak suggesting that desorption is the predominating process at high initial coverages. This is confirmed by the relatively small peak for N_2 desorption. In this respect, the results for the polycrystalline surface differ significantly from those for Rh{110}. On that rhodium surface, nitrogen desorption remained dominant even at highest coverages [6].

Another interesting observation is made for the high coverage conditions in panel (c) of fig. 2: a small oxygen desorption feature is found at $T_3 = 393$ K. This feature begins to appear at ~ 0.7 ML which corresponds to the same exposure that leads to the development of another nitrogen desorption feature at lower temperatures (ca. 420 K). On transition metals thermal desorption of oxygen after adsorption of either NO or O_2 usually occurs at much higher temperatures. For various rhodium single crystal surfaces desorption temperatures of at least 650 K have been reported [19–24]. The situation seems to be different for polycrystalline surfaces. Ho and White [25], however, have also reported on low-temperature oxygen desorption in an investigation of NO on Rh{100}. The authors explained the effect on the basis of a binding geometry, in which the NO molecule is bent over the surface leading to an interaction of both nitrogen and oxygen with Rh atoms and, consequently, to a weakened N–O bond. Due to the relatively high coverage of adsorbed species under the conditions of panel (c) a recombination of oxygen (nitrogen) atoms to gaseous O_2 (N_2) becomes possible.

In order to determine the kinetic parameters of NO dissociation, we have fitted a Polanyi–Wigner equation to the TPSSIMS data:

$$-\frac{\mathrm{d}\Theta}{\mathrm{d}t} = \nu\Theta^{n}_{\mathrm{NO}} \exp\left\{-\frac{E}{RT}\right\}. \tag{2}$$

Assuming an order of $n = 1$, a least-squares fitting procedure was applied to the results of several TPSSIMS rate curves obtained for different initial coverages. Fig. 3 shows the excellent agreement between the fitting result and the experimental data obtained for an NO exposure of 0.5 L and a heating rate of 0.52 K/s. Taking into account a variety of different measurements, we arrive at a value of $E = 8 \pm 2\,\text{kJ/mol}$ for the activation energy and $\nu = 10^{-0.2\pm0.4}\,\text{s}^{-1}$ for the preexponential factor. Since the experimental data are rather noisy, the fitting procedure seems to be the most reliable method for determining the kinetic parameters on the basis of eq. (2). For some of the less noisy results, however, we still tried to apply other methods which are commonly used to evaluate TPD spectra. For example, taking one specific spectrum, the method proposed by Chan et al. [26] resulted in $E = 7.7\,\text{kJ/mol}$ and $\nu = 10^{-0.35}\,\text{s}^{-1}$, while the method of Tronconi and Lietti [27] led to an activation energy of $E = 7.5\,\text{kJ/mol}$ and a similar preexponential. Both results agree well with those obtained by our fitting procedure.

3.3. ISOTHERMAL EXPERIMENTS

For our studies of isothermal dissociation the clean surface was first exposed to either 1.2 or 0.6 L of NO at a temperature low enough to avoid dissociation. The sample was subsequently heated to the desired temperature between 80 and 330 K. The evolution of the Rh_1NO_1^+ and Rh_1^+ ion intensities was monitored by SSIMS. As explained above, the ratio of $\text{Rh}_1\text{NO}_1^+/\text{Rh}_1^+$ directly reflects the NO coverage on the surface. The insert in fig. 4 gives the result for a temperature of $T = 183\,\text{K}$. In order to calculate a rate constant k for dissociation, an exponential decay, $\Theta_T(t) = \Theta_0 \exp\{-t/\tau\} + \Theta_r$, was fitted to the data (Θ_0 is the initial coverage, Θ_r is the remaining coverage in the case of incomplete dissociation, τ is the characteristic time for the dissociation process at a fixed temperature T, with $k = \tau^{-1}$). Fig. 4

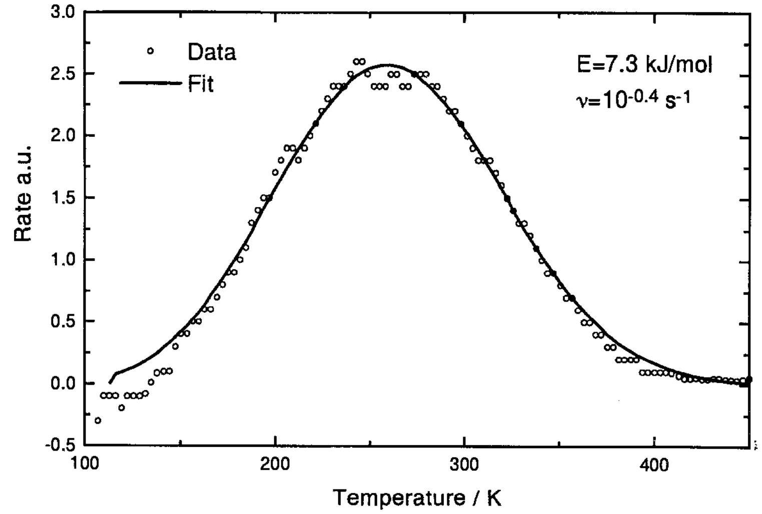

Fig. 3. TPSSIMS data fitted with a Polanyi–Wigner equation, NO exposure of 0.6 L, heating rate of 0.52 K/s, leading to kinetic parameters of 7.3 kJ/mol for the activation energy and $10^{-0.4}\,\text{s}^{-1}$ for the preexponential factor.

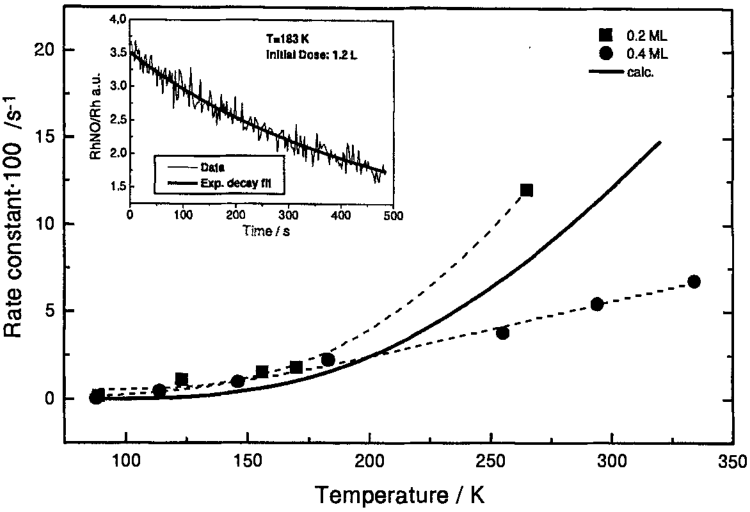

Fig. 4. Rate constants of two isothermal series with different initial exposures (0.56 and 1.2 L respectively). Each data point results from fitting with an exponential decay ansatz as shown in the insert. Both series are in good agreement with the previously obtained kinetic parameters. At higher coverages the rate constants are smaller due to site blocking by dissociation products.

shows the results obtained for the two series of isothermal measurements at different initial coverages in the temperature range from 80 to 330 K.

The rate constants are compared with the expected rate constants calculated for the whole temperature range on the basis of the kinetic parameters obtained by TPSSIMS. The agreement is again excellent. In particular, if compared to the rather broad range of uncertainty given by the margins of error of the TPSSIMS results, the isothermal rate constants are very close to the calculated curve.

It is also evident from fig. 4 that dissociation is slowed down considerably at higher coverage. The weaker temperature dependence of the rate constants under these conditions indicates that the reaction products cause a strong inhibiting effect on the dissociation process. The isothermal measurements at low coverages and temperatures were also used to confirm the static conditions of the SIMS experiments. They show that dissociation does not occur at these temperatures and coverages. This finding is in contrast to the results of Cautero et al. [28].

4. Conclusions

In the present investigation rate parameters for NO dissociation on a rhodium foil were determined by temperature programmed and isothermal static SIMS measurements. Values of $E = 8 \pm 2\,\mathrm{kJ/mol}$ for the activation energy and $\nu = 10^{-0.2\pm0.4}\,\mathrm{s}^{-1}$ for the preexponential factor were obtained. These parameters are similar to those of our previous TPSSIMS study of NO on Rh{110}, where we found an activation energy of $E = 15 \pm 2\,\mathrm{kJ/mol}$ and a preexponential of $\nu = 10^{1.9\pm0.5}\,\mathrm{s}^{-1}$. These results were confirmed in an independent investigation using Auger lineshape analysis [7]. Borg et al. [8] have recently published an investigation on Rh{111} employing TPSSIMS in an experimental approach similar to ours. The authors found that $E = 40 \pm 6\,\mathrm{kJ/mol}$ and $\nu = 10^{6\pm1}\,\mathrm{s}^{-1}$. All these findings are difficult to explain in terms of the transition state theory. There are still two other reports on quite "unusual" kinetic parameters for dissociation, i.e. CO/W{110} [29] and NO on K-promoted Rh{100} [2]. A variety of explanations were proposed. For example, Umbach and Menzel [29] considered low probabilities of in-phase motion of adsorbate-surface atoms. In our previous investigation on Rh{110} we also favored this idea in combination with a specific site geometry and a local move of rhodium atoms out of their equilibrium positions. N–O recombination on the other hand does not take place at temperatures of the dissociation process and thus cannot contribute to the observed kinetics. Another explanation for the low values of the kinetic parameters on the K-promoted Rh{100} surface involved an energy transfer from the decay of electron–hole pairs that might be created by electronic fluctuations at the surface [2,30].

Usually, NO dissociation at low coverages is considered a process of first-order kinetics. Since the dissociation of $\mathrm{NO_{ad}}$ requires at least one vacant adsorption site, a higher order process may result, depending on both the concentration of NO molecules and on the concentration of vacant sites. In fact, Borg et al. have used such an "ensemble" approach. In order to fit their data, they used a modified rate equation taking into account the participation of several rhodium atoms [8]. Depending on how many rhodium atoms are supposed to be involved, they arrive at different sets of kinetic parameters. Considering reasonable ensemble sizes their values always remain below those reported earlier for the Rh{111} plane [1].

Given the experimental evidence presently available, the kinetic parameters of NO decomposition on Rh depend on the surface orientation of the sample. The observation that the results on Rh{110} and on polycrystalline Rh are similar suggests the occurrence of a common decomposition mechanism on these surfaces. It is most likely that surface roughness plays an important role in this respect. If, on the other hand, comparison between different surface orientations is made on the basis of rate constants, it seems that a compensation effect is in operation. For a temperature of 300 K, the respective values are very similar for the single crystal surfaces, i.e. $k_{\{110\}} = 0.18\,\mathrm{s}^{-1}$ and $k_{\{111\}} = 0.11\,\mathrm{s}^{-1}$, while somewhat lower values are found for the polycrystalline Rh surface, i.e. $k_{\mathrm{poly}} = 0.025\,\mathrm{s}^{-1}$. Based on considerations of the spread of the data and the respective error propagations we found that the rate constants are not significantly different. Even if there are variations with the surface orientation, the effect seems to be rather small. More detailed conclusions will result from additional experimental work with other Rh single crystal surfaces.

Similarly (and possibly even more fundamental), the rather unusual rate parameters for NO dissociation call for clarification. As mentioned above, only qualitative arguments have been advanced so far. Accordingly, variable numbers of substrate atoms [8] or specific local geometries, as those associated with the presence of steps, have been considered to influence the dissociation kinetics. On Rh{110}, a surface reconstruction process may also come into play. Quite generally, if several elementary reactions take place quasi-simultaneously, the treatment of the data by means of a Polanyi–Wigner equation may not reveal the inherent dissociation kinetics of the NO molecule. Nevertheless, such an evaluation procedure will still be appropriate for kinetic modelling of consecutive reaction processes like the oscillating NO reduction on Rh which is a subject of research in our laboratory [13,15,20].

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