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Hysteresis and oscillations in the selectivity during the $NO–H_2$ reaction over Rh(533)

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The $NO–H_2$ reaction over Rh(533) shows oscillatory behaviour at H_2-rich mixtures in the 10^{-6} mbar pressure regime around 470 K. The selectivity changes periodically in time: the rate of N_2 formation is out of phase with the NH_3 and H_2O formation rates. Accumulation of atomic N plays a central role in the oscillating behaviour. A comparison will be made with the $NO–H_2$ reaction over Pt(100).

Keywords: $NO–H_2$ reaction; Rh(533); oscillations in selectivity

1. Introduction

The $NO–H_2$ reaction over Rh surfaces displays interesting non-linear behaviour under certain experimental conditions [1–4]. Spatiotemporal processes like chemical waves have been observed with PEEM over Rh(110) by Mertens and Imbihl [3] and over a Rh field emitter using field electron microscopy (FEM) [2]. These FEM results show that in the 10^{-6} mbar pressure regime oscillatory behaviour occurs around 470 K. Moreover, it was shown that this process is structure sensitive, i.e. not all the surfaces present on the tip take part in the oscillating wave.

Related to the FEM experiments where many surfaces are present in situ we were interested in investigating if oscillating behaviour could also be observed over isolated large Rh single crystal surfaces. In correspondence with the FEM results we could obtain oscillations in the rate of N_2 formation over Rh(533), a stepped $4(111) \times (100)$ surface, under similar experimental conditions [1]. Over a Rh(100) surface no oscillatory behaviour could be observed under these conditions. The absence of oscillatory behaviour over the Rh(100) surface can be explained by a build-up of strongly bound N on the surface during the NO–H_2 reaction under conditions were oscillations have been observed over Rh(533) [1]. NO can react with hydrogen to three N containing products, viz. N_2, NH_3 and N_2O and in this paper it will be shown that the selectivity also oscillates in time over the Rh(533) surface. The results will be discussed in comparison with similar results reported for the NO–H_2 reaction over Pt(100) [5–9].

2. Experimental

Two UHV systems were used in this study and both systems have been described earlier [1]. For the activity measurements a UHV system (base pressure 2×10^{-10} mbar) was used in a flow mode pumped by a turbo molecular pump and the mass spectrometer was differentially pumped by a small turbo molecular pump [1]. In this configuration the partial pressure changes as recorded with the mass spectrometer are linear to the reaction rates. To measure the temperature of the crystal either a Pt–PtRh or a chromel–alumel thermocouple was used. In order to minimize the contribution of the cracking product OH of H_2O (amu 17) in the NH_3 signal (amu 17), amu 16 (NH_2) was used instead of amu 17 to detect NH_3 formation. The AES experiments were done with a double pass CMA analyzer using an incident electron energy of 2.3 kV [10]. The current between sample and ground was always less than 0.4 μA. The pressure readings of the NO and H_2 gases on the ion gauge have been corrected for the ionization efficiencies assuming sensitivities relative for NO and H_2 to that for N_2 of respectively 1.3 and 0.5. The Rh(533) surface was cleaned using standard techniques like sputtering in Ar and heating in O_2, H_2 and subsequent flashing in UHV to 1400 K.

3. Results

Macroscopic rate oscillations during the NO–H_2 reaction over the Rh(533) surface have been observed in the 10^{-6} mbar pressure regime under H_2-rich H_2/NO ratios around 470 K. To obtain these oscillations the surface was heated and cooled down slowly (rate is 0.7 K/s) in the reaction mixture until a critical temperature was reached [1]. At this temperature the rate of formation of N_2 started to fluctuate and a transition took place between this unstable regime and a regime of regular rate oscillations. During the oscillations besides N_2 formation, also H_2O and NH_3 were detected. No N_2O as a reaction product has been observed. The product distribution during the oscillations as function of time is shown in fig. 1 at an NO pressure of 0.8×10^{-6} mbar and a H_2/NO ratio of about 14. The period of the oscillations is about 30 s. Not only the reaction rate but also the selectivity oscillates in time: the N_2 signal is out of phase with the H_2O and NH_3 signals. The NH_3 and N_2 signals are not exactly out of phase, a small delay exists of about 6 s.

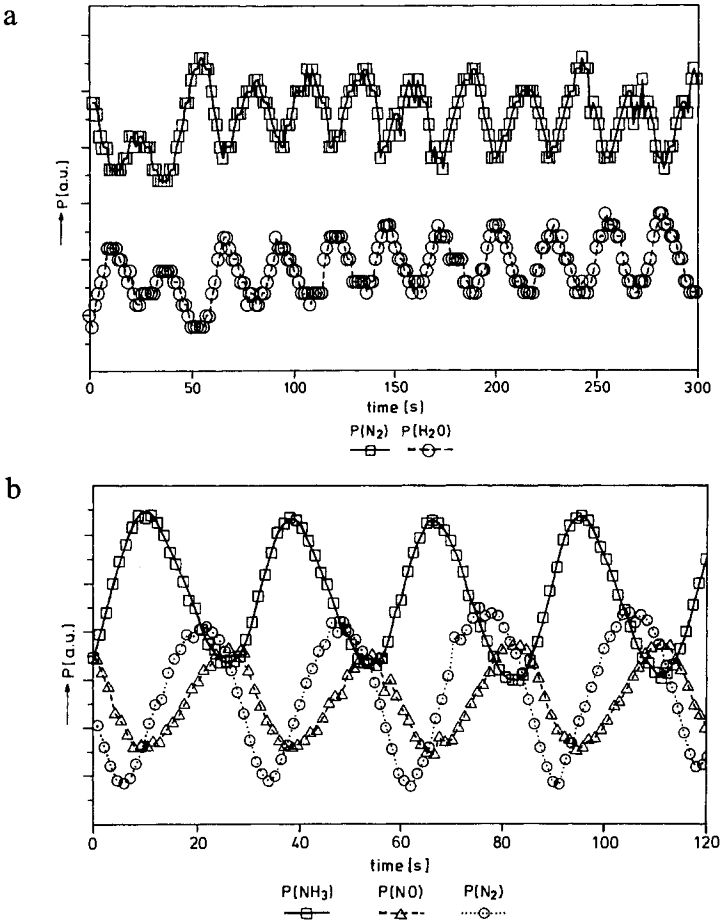

Fig. 1. (a) The N_2 (□) and H_2O (○) partial pressures as function of time at an NO pressure of 0.8×10^{-6} mbar and $H_2/NO = 14$, $T = 485$ K and (b) the NH_3 (□), NO (△) and N_2 (○) partial pressures as function of time at an NO pressure of 0.8×10^{-6} mbar, $H_2/NO = 14.5$, $T = 494$ K. Note that in this figure the mass spectrometer signals have been shifted vertically.

Figs. 1a and 1b were obtained at the same NO pressure and H_2/NO ratio but the temperature to find oscillations differed. After stopping the first experiment (fig. 1a) and subsequently starting a heat and cool run again, the temperature where oscillations occurred increased. Furthermore, it is important to note that once the oscillations have been obtained and the temperature is changed within 1 or 2 K the regular oscillations disappeared and the reaction rate behaved in an irregular manner. Besides the rates of formations of the three observed products N_2, NH_3 and H_2O, also the NO partial pressure oscillates in time as fig. 1b shows. The oscillating NO signal is a result of the consumption of NO during the reaction. The overall time averaged conversion of NO is rather low (below 10%). The NO signal is out of phase with both the NH_3 and H_2O signals. This indicates that at high consumption of NO (i.e. at a low NO signal) the rates of formation of H_2O and NH_3 are high. Thus, a direct relation exists between the conversion of NO and the production of H_2O and NH_3. No such relation exists between NO and N_2 in the oscillatory regime: the NO and N_2 signals are nearly in phase, a small delay between the maxima of respectively NO and N_2 is observed.

Upon heating and cooling in a H_2–NO mixture a hysteresis in the rate of formation of N_2 was observed. The hysteresis as a function of the H_2/NO ratio at an NO pressure of 3×10^{-7} mbar is shown in fig. 2. Above a H_2/NO ratio of about 8 some peaks appeared in the rate of N_2 formation during cooling down. Oscillations can be obtained at the high temperature side of these peaks [1]. At higher H_2/NO ratios (> 14) a new peak appeared during heating up and this peak increased in size as the H_2 pressure was increased. The temperature region and the temperature to find oscillations shifted to lower temperatures if the H_2 pressure was increased. A similar tendency has been observed if the NO pressure is lowered while keeping the H_2/NO ratio constant [1]. The data indicate that the hysteresis and the oscillations are related to each other. Therefore, a first step to clarify the mechanism of the oscillations is to monitor the species present on the surface during the hysteresis. For this purpose AES was used. Fig. 3 shows the AES intensity of the N peak (380 eV) and the O peak (510 eV) normalized to the Rh 256 eV peak versus the temperature in the presence of the reaction mixture at a H_2/NO ratio of 14.5 (a) and 15.3 (b) and an NO pressure of 7.2×10^{-8} mbar. These data were taken at steady state reaction conditions. Both the N or O and the Rh signals were measured

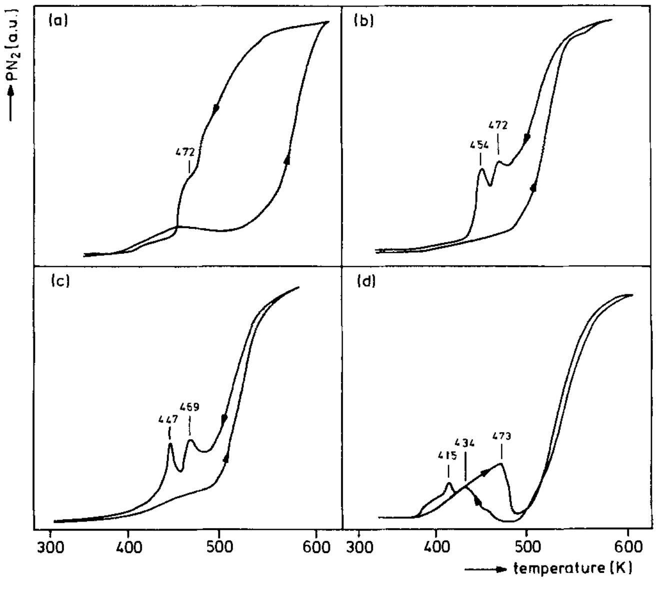

Fig. 2. Hysteresis in the rate of N_2 formation at an NO pressure of 3×10^{-7} mbar and H_2/NO ratios of respectively (a) 5.2, (b) 7.8, (c) 10.4 and (d) 30.

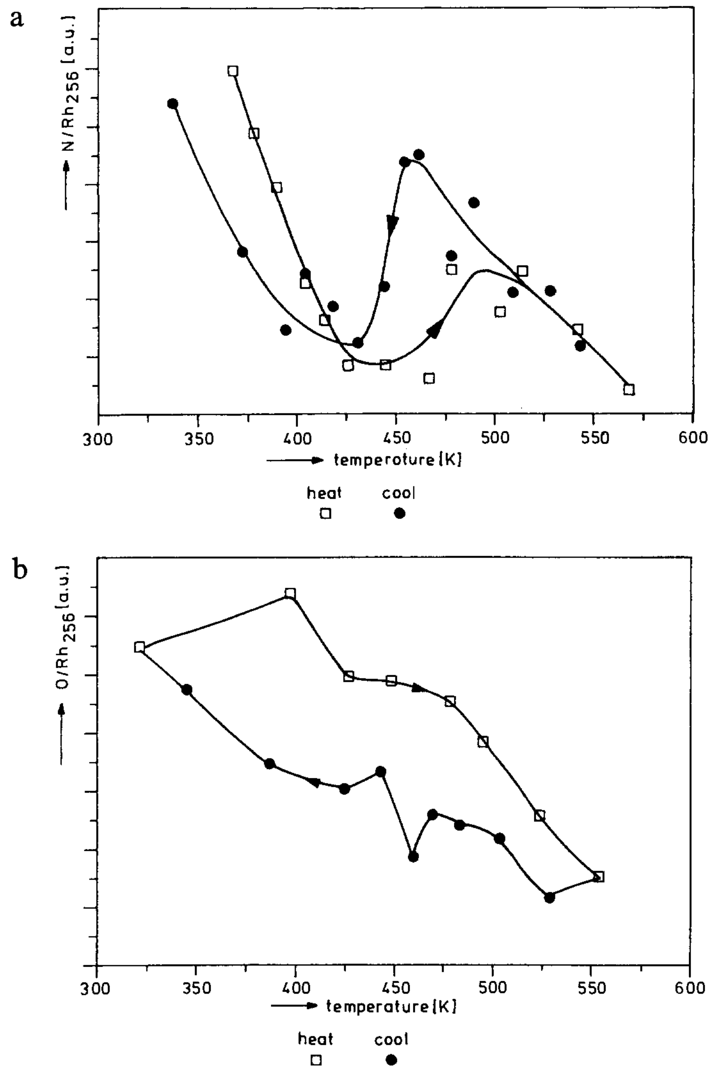

Fig. 3. (a) The N/Rh(256) AES ratio upon heating (□) and upon cooling (●) at an NO pressure of 7.2×10^{-8} mbar at a H_2/NO ratio of 14.5 and (b) the O/Rh(256) AES ratio upon heating (□) and upon cooling (●) at an NO pressure of 7.2×10^{-8} mbar at a H_2/NO ratio of 15.3.

simultaneously at a constant temperature and constant NO and H_2 pressures. Using AES we were limited to use NO pressures below 10^{-7} mbar but at these pressures still a hysteresis could be observed. In the range of the H_2/NO ratios used in this experiment the hysteresis in the N_2 reaction rate did not change. The N/Rh AES signal shows a hysteresis during heating and cooling the sample in the reactant mixture. Moreover, the local maximum on the cooling branch around 450 K coincides with the peak in the N_2 reaction rate observed while cooling down. The O AES signal also shows a hysteresis but contrary to the N peak the O peak stays at a low level on the cooling branch compared to the heating branch between 450 and 500 K.

To ensure that the influence of the electron beam upon the results could be neglected two experiments were performed. Firstly, a second heat and cool cycle was taken immediately after the first cycle and the AES results were similar to the results obtained in the first cycle. Secondly, by means of TDS the amount of N on the surface during the hysteresis was detected. The sample was heated or cooled slowly (<1 K/s) in the H_2–NO mixture to a chosen temperature. At this temperature the H_2–NO mixture was pumped off quickly followed by a TDS run. In all the TDS runs it was ensured that the influence of the background was the same. Therefore, the differences in the TDS spectra are related to differences in the surface composition during reaction between the two chosen temperatures. These data obtained show an increase of the N_2 TDS peak in the hysteresis region on the cooling branch. Thus, based upon the data obtained in the AES and the TDS experiments it can be concluded that the influence of the electron beam is small and can be neglected in the temperature region of interest.

4. Discussion and conclusion

To understand the mechanism of the oscillating behaviour of the NO–H_2 reaction over Rh(533) knowledge about the species present during the hysteresis in the N_2 reaction rate is necessary. The AES data taken in a NO–H_2 mixture show that also a hysteresis occurs in the N and O AES signals. Moreover, both signals behave in an opposite way: on the cooling branch between 500 and 430 K the N peak shows a local maximum while the O peak stays at a low level. In this temperature range the N AES signal on both the heating and cooling branch exactly follows the rate of N_2 formation. The increase in the N AES signal during cooling down can be attributed to the accumulation of a N containing intermediate like NO_{ads}, NH_{ads} [10] or N_{ads}. The N AES signal was rather a broad peak, therefore, no distinction could be made between NO, NH_{ads} and atomic N [11]. Since the temperature of the oscillating regime lies above the desorption temperature of NO (410 K) we attribute the N AES signal to either NH_{ads} or N_{ads}. In the presence of H_2 and provided enough vacancies on the surface are present atomic N is very likely to accumulate on the surface via the following overall reaction [12]:

$$NO + H_2 \rightarrow N_{ads} + H_2O \qquad (1)$$

Therefore, the O and N AES signals behave out of phase in the region where N is being accumulated.

Based upon the AES data a model can be constructed to describe the hysteresis in the N_2 formation rate. At room temperature the surface is saturated with mainly NO_{ads}, some N_{ads} and some H_{ads}. Heating the surface up to 430 K NO_{ads} starts to desorb and vacancies are created and the dissociation of NO is favoured. At this stage some O accumulates and the O AES signal stays at a high level while the N AES signal decreases. Above 430 K enough vacancies are created by the desorption of NO and the reaction rate increases and N is accumulated via reaction (1). Around 500 K N_2 starts to desorb [1] and the reaction rate increases rapidly. Upon cooling from 500 to 450 K, i.e. below the desorption temperature of N_2, atomic N is able to accumulate via reaction (1), probably in the form of islands [13]. In these islands the

$$N_{ads} + N_{ads} \rightarrow N_2 \tag{2}$$

reaction is favoured [13,14]. Below 450 K the dissociation of NO and the reaction between oxygen and hydrogen slow down and atomic O builds up. At this critical temperature the accumulation of N is inhibited and the N AES signal drops. At even lower temperature NO adsorbs again and the N AES intensity increases again.

If the accumulation of N is important in the hysteresis we can expect that it also may play an important role in the oscillating behaviour since the two processes are related to each other. During the oscillations the Rh(533) surface is reversibly poisoned by N atoms causing the observed bistability in the reaction rate. This process must be reversible because if the Rh–N bond strength becomes too strong the surface will be simply blocked by atomic N in the temperature regime where oscillations have been observed. This has been observed for Rh(100) [1]. The ability of the Rh(533) surface to accumulate atomic N during the NO–H_2 reaction explains the observed selectivities to N_2, NH_3 and H_2O. If the reaction is more selective to N_2 the coverage of N atoms is relatively high and, consequently, the concentration of vacancies is low. However, for the production of NH_3 and H_2O a relatively high concentration of vacancies is needed to dissociate both NO and H_2. Not only the rate of N_2 formation but also the rate of NH_3 formation shows a hysteresis during a heat and cool run. It is important to note that during cooling the NH_3 reaction rate reaches its maximum just before the N_2 reaction rate starts to increase. From this we conclude that the NH_3 and N_2 formation are in competition and that the NH_3 production is favoured at slightly higher temperatures because of a higher concentration of vacancies at this temperature.

Over Pt(100) also rate oscillations have been observed in the 10^{-6} mbar pressure regime around 460 K [5–9]. A vacancy model has been proposed by Siera et al. [5] to explain their results. Upon comparison of the results reported for Pt(100) [5] with the results obtained over Rh(533) some differences are remarkable. Contrary to Rh(533) over Pt(100) a so-called surface explosion [15] during heating in the H_2/NO mixture has been observed around 450 K and during the oscillations the N_2 signal is in phase with the NH_3 and H_2O signals. Not only the formation of NH_3 and N_2 but also the formation of N_2O has been detected and N_2O is out of phase with N_2 and NH_3. The differences can be understood by differences in properties of Pt(100) and Rh(533) in the NO–H_2 reaction. Over Pt(100) the dissociation of NO is the rate determining step in the reaction and the dissociation of NO proceeds in an autocatalytic way: once vacancies are created the dissociation of NO is initiated and in the presence of hydrogen, NH_3, H_2O and N_2 are formed including vacancies. The reaction rate accelerates and a sharp increase in the N_2 rate is observed around 450 K, a so-called surface explosion. The phase relationship of the products is like over Rh(533) related to the concentration of vacancies on the surface. At a low concentration of vacancies the dissociation of NO is inhibited and N_2O is formed via

$$NO_{ads} + N_{ads} \rightarrow N_2O \tag{3}$$

If the concentration of vacancies on the surface is large, the rate of dissociation of NO is high and the reaction is selective towards N_2, NH_3 and H_2O. No N_2O was detected over Rh(533) during the oscillations because of the low concentration of NO_{ads} under these conditions as a result of the fast dissociation of NO over Rh(533).

In summary, like over Pt(100) the NO–H_2 reaction rate and the selectivity oscillate in time in the 10^{-6} mbar pressure regime around 470 K. The mechanism of the observed oscillations in the selectivities, however, is different for the two surfaces: over Pt(100) the dissociation of NO is rate limiting while over Rh(533) the ability of the surface to accumulate N under H_2-rich H_2–NO mixtures plays a central role. Moreover, it has been reported that accumulation of atomic N over Pt(100) during the NO–H_2 reaction does not take place [12]. To understand the role of the (100) steps present on the Rh(533) surface it is planned to study the NO–H_2 reaction over a Rh(111).

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