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Oscillations in the N_2O-H_2 reaction over Ir(110). Route to chaos

Sónia A.C. Carabineiro^a, Wibo D. van Noort^b, Bernard E. Nieuwenhuys^{a,*}

 ^a Surface Science and Heterogeneous Catalysis Group, Leiden Institute of Chemistry, Leiden University, Einsteinweg 55, 2333 CC Leiden, The Netherlands
^b Philips Research Leuven, Kapeldreef 75, B-3001 Leuven, Belgium

Abstract

The study described in the present paper is focused on the N_2O-H_2 reaction on the Ir(110) surface and, in particular, on different kinds of oscillatory behaviour, including the route to chaos. Oscillations in rate were observed in the temperature range between 460 and 464 K, at a N₂O pressure of 1×10^{-6} mbar with H₂/N₂O ratios close to 1. Upon minor changes in the H₂/N₂O ratio, a series of period doublings is observed, resulting finally in aperiodic behaviour. © 2003 Elsevier Science B.V. All rights reserved.

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1. Introduction

NO reduction reactions and its oscillatory behaviour have been studied in detail on several metal surfaces because of its importance in automotive catalysis [1–13]. However less attention has been given to N₂O, which is an important greenhouse gas and it participates in cyclic reactions that lead to ozone destruction [14–18]. In a previous paper the oscillatory behaviour of the N₂O reaction with H₂ on the Ir(110) surface was described [19]. The present work deals with more recent results obtained with this surface that indicate different kinds of oscillatory behaviour, including the route to chaos.

However, proving that a given time series results from chaotic, rather than noisy, irregular or multi-periodic behaviour is far from trivial [4,20]. Chaotic behaviour is not just any kind of disorder; it appears to be completely unpredictable (equivalent to aperiodicity), but nevertheless obeys deterministic laws [4,20,21]. The experimental history of the system is essential to distinguish between chaotic and a noisy behaviour. The observation of period doublings in the oscillatory signals (where a single period is replaced by two, four, or eight periods and more) is a strong indication that a system is moving towards chaotic behaviour where periodicity is no longer present. That is to say that the system first starts to exhibit a one period one amplitude/shape oscillation and will start to exhibit

^{*}Corresponding author. Address: Faculty of Mathematics and Sciences, Gorlaeus Laboratories, Leiden University, Einsteinweg 55, P.O. Box 9502, 2300 RA Leiden, The Netherlands. Tel.: +31-71-527-4545; fax: +31-71-527-4451.

E-mail addresses: s.carabineiro@chem.leidenuniv.nl (S.A.C. Carabineiro), b.nieuwe@chem.leidenuniv.nl (B.E. Nieuwenhuys).

one large and one small amplitude/shape oscillation, which will repeat every cycle. The same will be true for the second period doubling, except that then the system will have four different amplitudes/ shapes. Period doublings can continue until finally a transition occurs to non-systematic variations in amplitude/shape, a state of so called "deterministic chaos". Moreover, very small perturbations are sufficient to induce these doublings, and the intensity of the chaotic signal is comparable to the ones of previous period doublings, which excludes the possibility that the system simply goes (gradually) into an extremely noisy regime.

Grassberger and Procaccia used correlation integrals that facilitate determination of the minimum number of variables that are required to describe the system mathematically, which can give valuable information for determining a reaction scheme [22–24]. Periodic and aperiodic oscillations can be distinguished by examination of the Fourier transformation of a measured time series (i.e., the power spectrum) [1,2,4,21,25].

In high pressure studies, the chaotic behaviour has been identified for massive metallic [26] and supported catalysts [27,28]. In low pressure single crystal surface studies, chaos has been demonstrated only for a few systems: $Pt(1\ 1\ 0)/CO + O_2$ reaction [25,29], $Pt(1\ 0\ 0)/NO + H_2$ [1,2], $Pt(1\ 0\ 0)/$ NO + NH₃ [2–4], $Pt(1\ 0\ 0)/NO + CO$ [30–33]. In all those systems, a transition from regular oscillations to chaos took place via the sequence of period doublings described above, i.e., the Feigenbaum scenario. By stepwise changing the pressure of one of the reactants in these systems, the oscillations undergo transitions from periodic to aperiodic (or chaotic) behaviour through a sequence of period doublings.

2. Experimental

Measurements were carried out in a UHV system with facilities for LEED, AES and quadrupole mass spectrometry. Further details of the experimental set-up, preparation of the Ir(110) surface, and the procedure used for the mass spectrometric analysis of reactant and reactions are described elsewhere [19].

3. Results and discussion

In a previous paper, it was shown that in the temperature range between 460 and 464 K, rate oscillations were observed at a N₂O pressure of 1×10^{-6} mbar, with H₂/N₂O ratios close to 1 [19]. The procedure to obtain those oscillations is described in the same paper, and consists of heating the crystal in N₂O with a very low amount of H₂, from room temperature to 800 K and cool it down to the temperature expected for oscillations and then increase stepwise the pressure of H₂ until sustained oscillations start [19].

In the present work, oscillatory behaviour was established at a constant temperature (461 K), through the procedure described above. Once oscillations started, it was shown that a tentative change in the H₂ pressure resulted in loss of the oscillations. In contrast, small changes in the pressure of N₂O (originally 1×10^{-6} mbar) resulted in changes in the oscillatory behaviour. These changes were very small (around 1%), sometimes hardly noticeable by the ion gauge. With an initial H_2/N_2O ratio of 1.4, upon those slight changes in the N2O pressure, a series of period doublings was observed, finally resulting in aperiodic behaviour (Fig. 1). Fig. 1a shows a sequence of all kinds of behaviour observed: It started with period-1 oscillations (I). Then upon minor changes in the H2/N2O ratio, a series of period doublings was obtained: period-2 (II), period-4 (III) and period-8 (IV). Finally, another minor change in the N₂O pressure resulted in aperiodic behaviour (V). During all those changes the system took only a few periods to reach a new "steady-state" oscillatory behaviour (this intermediate periods are not shown in Fig. 1a. Instead, to make it simpler, gaps in pressure and the time scale are shown). Those five types of oscillatory behaviour (single period, period-2, period-4, period-8, aperiodic) are shown in detail in Fig. 1b-f, respectively. The transition between oscillatory states were shown to be completely reversible (by a "reverse" change in the N₂O pressure), but only between the periods 1, 2, 4 and 8. Once in the aperiodic "zone", reversion was not possible anymore. Moreover, these oscillations are very sensitive to experimental factors and fade away easily,



Fig. 1. Oscillations in the partial pressures of H_2O and N_2 , at a starting N_2O pressure of 1×10^{-6} mbar, at 461 K and a H_2/N_2O ratio of 1.4. A sequence of all kinds of oscillatory behaviour found is shown (a). The oscillations show first: (I) single period behaviour (b), followed by a series of period doublings: (II) period-2 (c), (III) period-4 (d), and (IV) period-8 (e), resulting finally in: (V) aperiodic behaviour (f).

which is shown in the last part of Fig. 1a. Oscillatory behaviour thus ended spontaneously, starting by a decrease in the amplitude of oscillations and finally total loss of oscillations (a completely straight line). This made it impossible to obtain more points for the aperiodic "zone". The oscillations could only be triggered again by heating the crystal up to 800 K and cooling down to the desired temperature (around 460 K), as described to obtain them [19]. This procedure could always be used to recover oscillatory behaviour, if oscillations faded away.

The correlation integrals were calculated according to the method described by Grassberger and Procaccia [22–24]. The results obtained by this method were inconclusive, due to the limited number of points that were available. Obtaining more points is hampered by the difficulty to sustain these oscillations for an extended period of time. The Fourier-transform power spectra of the time series were also obtained (Fig. 2). The power spectrum of a period-1 oscillation revealed the main frequency (Fig. 2a). In the power spectra of the period-2 (Fig. 1b), period-4 (Fig. 1c) and period-8 (not shown) oscillations, higher order frequencies appeared. Finally, for the aperiodic oscillations (Fig. 1d), several frequencies appeared in the Fourier-transform power spectrum, giving it a "noisy" appearance. Similar results were obtained by other authors [1,2,4].

Period-3 and period-5 oscillations were obtained by the same authors while searching for the chaos in other reactions [1,2,4]. Here, this type of oscillations was also observed, as is shown in Figs.



Fig. 2. Power spectra of single period oscillations (a), period-2 (b), period-4 (c) and aperiodic oscillations (d) in the N₂ partial pressure.



Fig. 3. Three period oscillations in the N₂O partial pressure, at a pressure of 9.85×10^{-7} mbar N₂O, at 460 K, and a H₂/N₂O ratio of 1.42 (a). The corresponding power spectrum is shown (b).

3 and 4, for N_2O and N_2 pressures, respectively. It can be observed that the total period of this kind of oscillations (Figs. 3a and 4a) was not much different from the period-2 and period-4 oscillations (Fig. 1c and d), that is 2.7 ± 0.2 min and 5 ± 0.2 min, respectively. However, by observation of the power spectrum of period-2 (Fig. 2b) and period-3 oscillations (Fig. 3b), it can be seen that the main frequency changed from 0.55 to 0.25 Hz and that other overtones appeared (2ω and 4ω). As for the differences between the power spectra of period-4 (Fig. 2c) and period-5 (Fig. 4b) oscillations, it can be seen that the main frequency is maintained, however the frequency at $5/3\omega$, disappears and is replaced by another one at $4/3\omega$. The frequency at $2/3\omega$ becomes smaller and also an additional overtone appears at 2ω .

The number of points needed to describe a single period oscillation is 12. For the first period doubling, the number of points needed to describe a double period oscillatory cycle is 25. Moving further, the amount of points needed to describe



Fig. 4. Five period oscillations in the N_2 partial pressure, at a pressure of 9.75×10^{-7} mbar N_2O , at 460 K, and a H_2/N_2O ratio of 1.44 (a). The corresponding power spectrum is shown (b).

each period doubling increases, resulting in longer cycles. For the aperiodic regime, no repeating cycle was found, at least within the limits of the experimental data. The observed period doublings, and the extremely small pressure differences associated with them, strongly indicate that a route to chaos was observed, which is further emphasized by the "zone" where no periodicity was found.

Fig. 5 shows the first 8 min of oscillations at 463 K. It can be seen that N_2O oscillates in counterphase with N_2 and the maxima in H_2O formation are "delayed" compared to the maxima of N_2 formation. That relationship had already been pointed out in the previous paper [19]. The following steps were proposed as part of the mechanism:

$$N_2 O_{(g)} \rightarrow N_{2(g)} + O_{ads} \tag{1}$$

$$H_{2(g)} \rightarrow 2H_{ads}$$
 (2)

$$O_{ads} + 2H_{ads} \rightarrow H_2O_{(g)}$$
 (3)

The model is based on different rates of O_{ads} removal by (3), formation of O_{ads} by (1) and a large



Fig. 5. Detail of oscillations in the partial pressures of N₂O, H₂O and N₂, at 463 K. N₂O pressure of 1×10^{-6} mbar and H₂/N₂O ratio of 0.9. The N₂O conversion was 7%.

effect of O_{ads} on the N_2O dissociation (1). A buildup of atomic oxygen on the surface (observed by AES), has a large effect on the rate of N_2O dissociation, until oxygen is released in the form of water. Rate oscillations for the N_2O-H_2 reaction are related to periodic transitions between O-rich and O-poor surfaces [19]. Work is being carried out in order to model these reactions [34]. It has been shown that the unusual phase shift between production rates of N_2 and H_2O (Fig. 5) is closely connected with the character of lateral interactions in the adlayer [34]. At a certain stage, hydrogen removes the oxygen from the surface, resulting in H_2O production and affecting the dissociation of N_2O [19,34].

4. Conclusions

Oscillations in rate were observed for the N₂O– H₂ reaction over Ir(110), at a N₂O pressure of 1×10^{-6} mbar, with H₂/N₂O ratios close to 1, from 460 to 464 K. Upon a little change in the H₂/N₂O ratio, a series of period doublings is observed, which result finally in aperiodic behaviour. These observed period doublings and the extremely small pressure differences associated with them are a strong indication that a route to chaos for this reaction was observed.

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