Mathematical Modelling of Oscillatory Behaviour during $N_2O + H_2$ Reaction over Ir (110)

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Abstract

A mathematical model is presented, which simulates the oscillatory behaviour reported for the N_2O+H_2 reaction over Ir (110) surface. The model describes successfully the very narrow temperature range for the appearance of oscillations and the properties of oscillations including their period and the waveform. The presented model also can simulate the phase shift, between the maxima of H_2O and N_2 production rates, which has been detected experimentally. It is demonstrated, that this unusual phase shift between production rates of two reaction products is closely connected with the character of lateral interactions in the adlayer.

1. INTRODUCTION

Oscillatory behaviour during the $NO + H_2$ reaction has been widely studied over Pt, Rh and Ir single crystal surfaces and a review of these studies can be found in ref [1]. The reaction of $NO + H_2$ was the first oscillatory system, where the problem of the understanding of oscillations in selectivity was arisen. Two of three possible products, namely N_2 and NH_3 were oscillating with different phase shifts for various single crystal surfaces. While for Pt(100), Ir(100) and Ir(510) N_2 and NH_3 were oscillating in phase, there was the phase shift between the N_2 and NH_3 production rates over Rh(111), Rh(110), Ir(110) and Ir(210) single crystal surfaces. Mathematical modelling was used to understand the mechanism of the non-linear behaviour of the $NO + H_2$ reaction over Pt(100) [2–4] and Rh(533), Rh(111) [5] single crystal surfaces. It was demonstrated, that the anti-phase oscillations in the N_2 and NH_3 production rates could be explained on the basis of the character of the lateral interactions between adsorbed species [5].

Less studies were devoted to the $N_2O + H_2$ reaction over noble metal surfaces and only recently self-sustained reaction rate oscillations in this system were discovered over the Ir(110) surface [6]. The oscillatory behaviour was found in the narrow temperature range between 460 K to 464 K at a N_2O pressure of 10^{-6} mbar with H_2/N_2O ratios close to 1. The period of oscillations was about 60 s. The reaction products were N_2 and H_2O. N_2O oscillates in anti-phase with N_2 and the maxima in H_2O formation were "delayed" compared to the maxima in N_2 formation during the oscillations. The goal of the present study is the development of a mathematical model, which can describe the experimentally observed oscillatory behaviour and to explain the origin of the phase shift between oscillations in N_2 and H_2O production rates.

2. EXPERIMENTAL

Reactions were performed in a UHV system (Leybold Heraeus) equipped with facilities for LEED, AES and a differentially pumped (60 l/s)

quadrupole mass spectrometer (UTI 100 C). The system was pumped by a turbo molecular pump (170 l/s) and an ion pump (150 l/s). The base pressure was always better than $2\ 10^{-10}$ mbar. The crystal was cleaned by repetitive cycles of heating in an oxygen or hydrogen atmosphere, Ar^+ ion sputtering (p(Ar) = $1\ 10^{-5}$ mbar, incident energy = 1.5 kV) and flashing in UHV to 1400 K. The Ar^+ ion sputtering and flashing treatments were repeated at the beginning of each series of experiments and the surface cleanliness was checked by AES and LEED. Further details about the experimental procedure are described elsewhere [6].

The oscillations were obtained by slowly heating the crystal in N_2O ($1\ 10^{-6}$ mbar) with a very low amount of H_2, the smallest possible to be read on the ion gauge (resulting in a H_2/N_2O ratio of approximately 0.4) from room temperature to 800 K and then cool it down to a temperature between 450 K and 470 K. Then the pressure of H_2 was increased stepwise until sustained oscillations in rate started. Figure 1 shows oscillations in the partial pressures of N_2O, H_2O and N_2, which were detected at 460 K for a N_2O pressure of $1\ 10^{-6}$ mbar and H_2/N_2O ratio of 1.2.

As can be seen from this figure, the product N_2 pressure oscillates in anti-phase with the reactant N_2O pressure, as can be expected. However it can also be noted that the oscillations in H_2O formation are "delayed" compared to the oscillations in rate of N_2 formation. The oscillations are very sensitive to changes in the H_2/N_2O ratio or temperature, fading away easily.

AES measurements were also carried out during the oscillations. For that purpose the rate oscillations were started and the crystal was taken away from the front of the MS hole to the front of the CMA hole. Since the period of oscillations is of the order of 1 min and a full AES spectrum takes about 2.5 min, the evolution of the oxygen peak (O_{510eV}) could not be followed during one oscillation cycle. However it was observed that the O-concentration varies from zero to a maximum value during the rate oscillations [6].

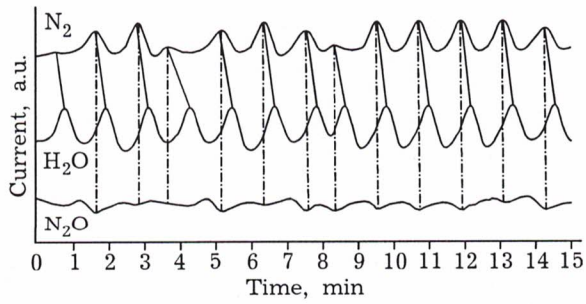

Fig. 1. Oscillations in the partial pressures of N_2O, H_2O and N_2, on the Ir(110) surface, at a N_2O pressure of $1\ 10^{-6}$ mbar. The temperature was 460 K and the H_2/N_2O ratio was 1.2. From reference [6].

3. MATHEMATICAL MODELLING AND DISCUSSION

The TDS studies revealed some interesting features of this system [6]. Usually adsorption of N_2O over metals such as Pt and Rh results in the formation of N_2 and O_{ads} on the surface, whereas on the more active metal surfaces also N_{ads} can be detected. However TDS studies showed that on Ir(110) only N_2 and N_2O were released from the surface in the temperature range from 350 K to 500 K and no NO desorption was detected. In addition it was demonstrated, that oxygen could modify the rates of N_2O desorption and decomposition in a very complicated manner. At small oxygen precoverages, N_2O decomposition is accelerated by oxygen, while at higher oxygen coverages a large increase in the N_2O desorption peak with increasing O precoverage was identified (see Fig. 2, *a* from ref. [6]). It was concluded that the presence of oxygen on the surface could modify the N_2O desorption rate.

To model the experimental observations the following set of elementary steps was formulated:

$$N_2O_{(g)} + [M] \underset{k_{-1}}{\overset{k_1}{\Leftrightarrow}} [M{-}N_2O]$$

$$[M{-}N_2O] \overset{k_2}{\Rightarrow} N_{2(g)} + [M{-}O] \qquad (1)$$

$$H_{2(g)} + 2[M] \underset{k_{-3}}{\overset{k_3}{\Leftrightarrow}} 2\,[M{-}H]$$

$$[M{-}O] + 2\,[M{-}H] \overset{k_4}{\Rightarrow} H_2O_{(g)} + 3\,[M]$$

The reaction mechanism includes the adsorption/desorption of N_2O, H_2 and N_2O dissociation. According to the data of TPD studies [6] the reaction products N_2 and H_2O produced

TABLE 1

Parameter	k_1	$\tilde{k}_{-1}$	$\tilde{k}_2$	k_3	k_{-3}	k_4
k_0^*	$6.2\ 10^4$	10^{12}	$5.0\ 10^{22}$	$8.3\ 10^5$	$2.58\ 10^8$	$3.04\ 10^6$
E, cal/mol	0	35000	51700	0	23000	15000
k^{**}	0.062	0.001	0.014	1	0.003	0.225

*Dimension of k_1 and k_3 is $(s\ mbar)^{-1}$, dimension of k_i for $i = -1, 2, -3$ and 4 is s^{-1}.

**The value of the constant at $p_1 = 10^{-6}$ mbar, $p_3 = 1.2\ 10^{-6}$ mbar, and $T = 460$ K.

The parameters of lateral interaction energies in the rates k_{-1} and k_2 were chosen as $\mu_{-1} = -3640$ cal/mol, $\mu_2 = -9100$ cal/mol, so that at $T = 460$ K, $\varepsilon_{-1} = 4$, $\varepsilon_2 = 10$.

at $T > 400$ K desorb immediately after their formation on the catalyst surface.

Mathematical modelling has been done on a macroscopic level and is based on the standard mean field approximation. The nonideality of the adsorbed layer was accounted for through the parameters of lateral interactions ε_α where α denotes the number of the step. For the developing of the mathematical model the following assumptions are made:

1) H_2 and N_2O adsorption proceed on separate sub-lattices of surface adsorption centres;

2) each adsorbate can occupy only one site on the sub-lattice and the species compete for free sites only on the same sub-lattice;

3) on a microscopic scale a randomly well-mixed adlayer is formed in spite of lateral interactions;

4) the variations of the gas phase partial pressures P_{N_2O} and P_{H_2} are very small during the reaction.

Following the proposed reaction mechanism, one arrives at a set of three coupled ordinary differential equations (ODE), describing the temporal variation of surface coverages during the reaction:

$$\begin{aligned} \dot{x} &= p_1 k_1 (1 - x - y) - k_{-1} x - k_2 x \\ \dot{y} &= k_2 x - k_4 y z^2 \\ \dot{z} &= p_3 k_3 (1 - z)^2 - k_{-3} z^2 - k_4 y z^2 \end{aligned} \qquad (2)$$

where p_1 and p_3 are the partial pressures of N_2O and H_2 and x, y, z denote the coverages of N_2O, O, and H.

Mathematical analysis demonstrates, that there is no any limit cycle solutions in the system (2) at any values of the constants k_i, where $i = \pm 1, 2, \pm 3, 4$. The origin of oscillations in this system is supposed to be due to the lateral interactions existing in this system. The analysis of the TPD spectra presented in ref. [6] demonstrates that oxygen greatly modifies the rates of N_2O desorption and dissociation. It was supposed, that due to lateral interactions adsorbed oxygen accelerates the rate of N_2O desorption and the rate of N_2O dissociation. A linear dependence of the activation energies of the following steps on the oxygen coverages were introduced in the model (2) as $E_{-1} + \mu_{-1} y$ and $E_2 + \mu_2 y$ where $\mu_{-1}, \mu_2 < 0$. The nonlinearity, which is necessary for the production of rate oscillations in the system (2) is presented via the dependence of the rate constants k_{-1} and k_2 upon the oxygen coverage: $k_{-1} = \tilde{k}_{-1} \exp(\varepsilon_{-1} y)$, $k_2 = \tilde{k}_2 \exp(\varepsilon_2 y)$.

The values of model parameters were chosen in such a way that they are in agreement with the known literature data and produce the best qualitative similarity of model solutions and experimental data. The obtained values of parameters are shown in the Table 1.

The results of the bifurcation analysis at the chosen values of parameters are presented in Fig. 2 that shows the phase diagram of

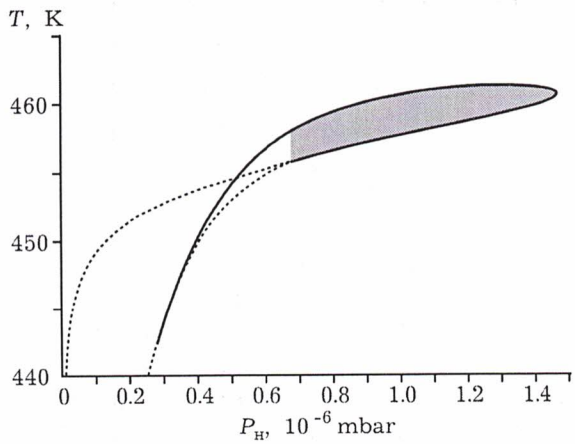

Fig. 2. The phase diagram of the model (2) at $p_1 = 10^{-6}$ mbar.

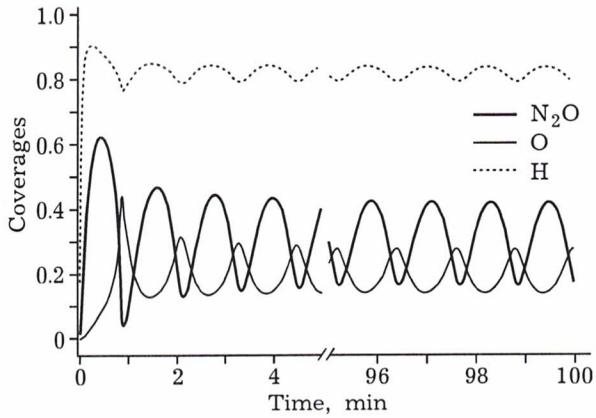

Fig. 3. Oscillatory behaviour of surface coverages at $p_1 = 10^{-6}$ mbar, $p_3 = 1.2\ 10^{-6}$ mbar and $T = 460$ K.

the system (2) in the plane (p_3, T). The solid line denotes the line of the Andronov–Hopf bifurcation and the dashed line represents the line of a saddle-node bifurcation. The region of oscillations is shown by the grey area. As can be seen from this Figure, the temperature region where oscillatory solutions originate is rather narrow. This fact is in excellent agreement with the experimental observations.

Figure 3 displays oscillatory behaviour of the coverages of the adsorbed species, obtained as a result of mathematical modelling. The period of oscillations and the conditions of their appearance closely coincide with the experimental data.

Figure 4 shows oscillations in the production rate of H_2O and in the rate of N_2O decomposition. The last value coincides with the rate of N_2 formation, because following experimental data N_2 molecules desorb immediately after their formation on the catalyst surface.

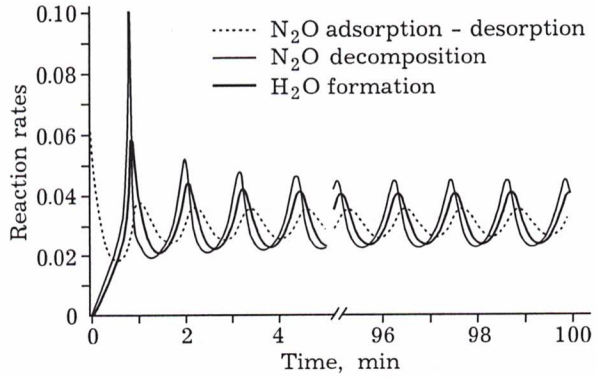

Fig. 4. Rates of N_2O decomposition and H_2O formation at the same conditions as in Fig. 3.

Figure 4 demonstrates that the results of mathematical modeling reproduce the experimental observations, including the observation that the oscillations in the H_2O formation rate are "delayed" compared to the oscillations in the rate of N_2 formation. The origin of this time delay is connected with the phase shift between the surface concentrations of N_2O and O as shown in Fig. 3. The mechanism of oscillations (see Fig. 3 and 4) may be presented as follows: starting with the clean surface, hydrogen immediately occupies all sites on its sublattice and hydrogen has a minor role in the appearance of oscillations. The concentration of N_2O on the surface increases. Due to the dissociation of N_2O the concentration of adsorbed oxygen increases. Oxygen accelerates N_2O dissociation and the N_2O surface concentration drastically decreases (solid line in Fig. 3), while the O coverage increases in a autocatalytic way. However, due to the reaction with hydrogen the concentration of surface oxygen starts to decrease. The decrease of the oxygen concentration causes an increase of the N_2O surface concentration. As the result of this process the rate of N_2O dissociation again increases, leading to an increase of the surface concentration of oxygen. Oxygen again accelerates the N_2O dissociation rate and the cycle of oscillations starts again.

4. CONCLUSION

A mathematical model is presented, which simulates the oscillatory behaviour reported for the $N_2O + H_2$ reaction over the Ir (110) surface. It is shown that lateral interactions in the adlayer can be the origin of the observed oscillatory behaviour. The character of lateral interactions was obtained from the analysis of the TPD spectra.

The results of the simulation demonstrate that nearly all peculiarities of the experimentally observed kinetic oscillations mentioned in Sec. 2, can be modelled rather well with the model presented in this paper. The model simulates successfully the very narrow tempera-

ture range for the appearance of oscillations and the properties of oscillations, including their period and the waveform.

The model presented simulates the phase shift, between the maxima of H_2O and N_2 production rates. It is demonstrated, that this unusual phase shift between production rates of two reaction products is closely connected with the character of lateral interactions in the adlayer. According to the proposed mechanism hydrogen plays a minor role in the appearance of oscillations by removing the oxygen from the surface, resulting in H_2O production. This result of the simulation is supported by the recent observation of isothermal sustained oscillations in the rate of N_2O–CO reaction. This observation demonstrates that the oscillations can be produced with different reducing agents [7].

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