CROATICA CHEMICA ACTA CCACAA **56** (1) 17—27 (1983)

YU ISSN 0011-1643
CCA-1352 UDC 546.11/.74:541.094.3
Original Scientific Paper

Mathematical Model of the Oscillatory Oxidation of Hydrogen on Nickel

Željko Kurtanjek

Faculty of Biotechnology, The University of Zagreb Pierottieva 6, 41000 Zagreb, Yugoslavia

Received February 26, 1982

The oscillatory states in the oxidation rate of H_2 on nickel were investigated by the CPD measurements. The oscillations were found in the range of temperatures 433—673 K and gas velocities 0.006—2.5 m/s. At gas velocities above 0.1 m/s oscillations in the catalyst temperature and gas composition disappeared while CPD oscillations remained, revealing the chemical cause of the oscillations. A mathematical model is proposed based on assumption of simultaneous oxidation and reduction of the surface. The model predicts oscillatory states and its predictions are in semiquantitative agreement with the experimental data.

INTRODUCTION

Heterogeneous catalytic reactions are known of exhibiting an intriguing variety of behaviour, such as multiple steady states, extinction and ignition phenomena, oscillations, and chaotic variations (flickering) of reaction rates. There has been renewed interest in such reaction systems, aside from possible practical implications, its intriguing quality requires detailed knowledge of physical and chemical processes, and without an appropriate mathematical model it can not be easily explained or anticipated. Most of the experimentally investigated oscillatory systems were conducted with oxidation reactions catalyzed either by supported catalyst or bulk metals such as wires, mesh, and plates. Works of R. A. Schmitz et al.[1] and W. H. Ray et al[2] contain up to date surveys of the experimental results. There is a rather strong indication that oscillations are not caused by interaction between transport and chemical rate processes but are due to complex surface interactions. M. Slinko et al.[3-6] investigated oxidation of H_2 on nickel and platinum and proposed that oscillations are due to linear dependence of activation energy of the surface reaction on oxygen coverage. D. Luss et al.[7] treated the problem with the same idea, and D. D. Bruns et al.[8] extended it by including various forms of functional relationships. G. Eigenberger[9,10] and R. Aris et al.[11] developed models assuming coverage independent parameters. However, their models include additional buffer steps like two forms of adsorbed species or a side reaction. A. T. Larson and F. E. Smith[12] were the first who brought up the possibility that instabilities in the oxidation of H_2 on nickel are caused by successive oxidation and reduction of nickel. Explaining experiments with supported platinum, palladium, and nickel foil, M. Boudart et al.[13] and R. A. Schmitz et al.[14,15] assumed oxidation of the catalyst. C. G. Vayenas et al.[16,17] concluded from direct measurements of O_2 activity on platinum in the oxidation of C_2H_4 that oscillations are caused by periodic formation and decomposition of platinum oxide. Aside from pure chemical theories of oscillations, recently K. F. Jensen and W. H. Ray[2,18,19] have proposed a pebbly surface model which predicts oscillatory solutions due to coupling of heat and mass transport with surface reaction.

EXPERIMENTAL

The reaction mixture of H_2 and O_2 was passed over a nickel catalyst made in form of a plate. The oscillatory states were investigated by simultaneous measurements of the contact potential difference (CPD), effluent gas analysis, temperature of the catalyst surface, and the temperature difference between the catalyst and surrounding gas. The reaction was studied in a once through flow reactor and in a recirculating reactor. The CPD was measured by the vibrating capacitor method (Kelvin's probe) and was used to help identification of adsorbed species under the reaction conditions. Upon adsorption of gas on catalyst surface, adsorbed species yield dipolar surface complexes, which may be charged negatively or positively outwards with corresponding increase or decrease of the electron work function. The vibrating capacitor method enabled measurements of the difference between the electron work functions (CPD) between two metals, the catalyst and the inert reference probe made of glass coated tungsten. Detailed description of the experimental system and procedure can be found in.[20-24]

RESULTS

The oscillatory states were observed over a wide range of temperatures (433—673 K) and gas velocities (0.006—2.5 m/s), containing large excess of H_2. Periodic oscillations were observed when mass and heat transfer limitations existed. Chaotic variations existed when transport resistances were negligible. Some of the recorded oscillations are shown in the Figure 1. At high velocities, above 0.1 m/s, oscillations in the gas phase and temperature disappeared, while CPD oscillations persisted, revealing oscillations in composition of adsorbed species on the surface. Experiments with adsorption and desorption of one of the reactants led to identification of the following adsorbed species:[21] clean nickel surface, chemisorbed H_2, chemisorbed O_2 with simultaneous transition to nickel oxide, and nickel oxide. In the Figure 2. are shown the CPD changes when partial pressure of O_2 was gradually increased from 0—2 kPa. Initially (without O_2) the surface is covered with chemisorbed H_2 producing negative dipole layer exposed outward. At low pressures ($pO_2 \leq 100$ Pa) the surface is largely reduced and covered with chemisorbed H_2 and O_2. Contribution of O_2 to the surface potential is more negative compared to H_2, resulting in decrease of the CPD with increase of pO_2. At $pO_2 \approx 100$ Pa a soft bifurcation to an oscillatory state occurs. In the range of pressures of 0.1—1 kPa autonomous oscillations are obtained. The second bifurcation occurs at about 1 kPa. The oscillations disappear as a soft bifurcation and the CPD reaches the plateau. Further increase of pO_2 to about 10 kPa does not result in appreciable CPD changes.

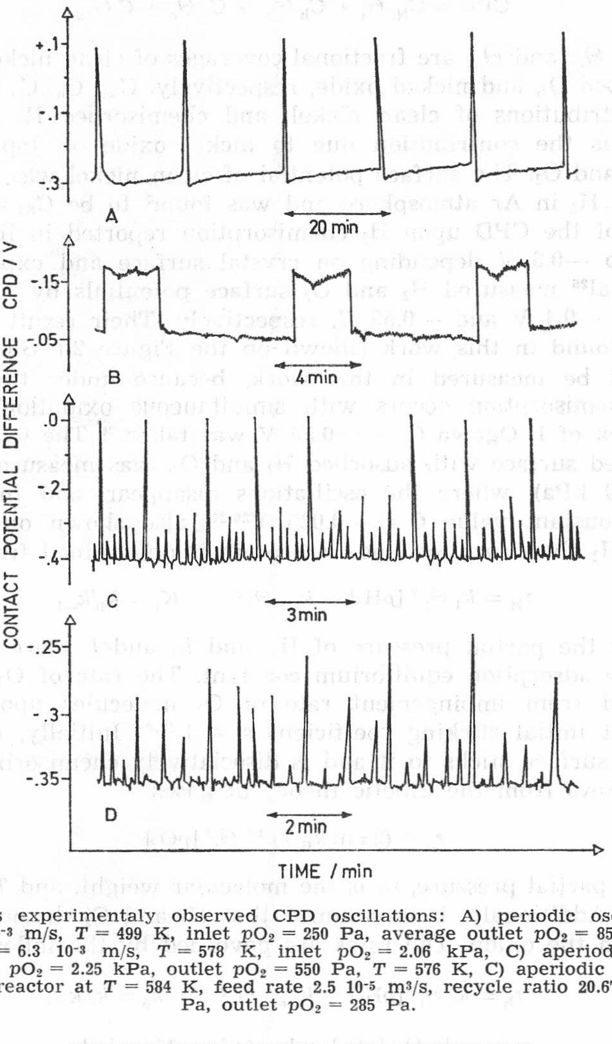

Figure 1. Various experimentaly observed CPD oscillations: A) periodic oscillations at gas velocity $v = 6.9\ 10^{-3}$ m/s, $T = 499$ K, inlet $pO_2 = 250$ Pa, average outlet $pO_2 = 85$ Pa, B) periodic oscillations at $v = 6.3\ 10^{-3}$ m/s, $T = 578$ K, inlet $pO_2 = 2.06$ kPa, C) aperiodic variations at $v = 0.26$ m/s, inlet $pO_2 = 2.25$ kPa, outlet $pO_2 = 550$ Pa, $T = 576$ K, C) aperiodic CPD attained in the recirculating reactor at $T = 584$ K, feed rate $2.5\ 10^{-5}$ m^3/s, recycle ratio 20.67, inlet $pO_2 = 350$ Pa, outlet $pO_2 = 285$ Pa.

MATHEMATICAL MODEL AND DISCUSSION

The catalyst has a nonuniform polycrystaline surface composed of individual patches each having different work function and different surface potential changes after adsorption. For Kelvin type CPD measurements it is reasonable to assume that the probe senses the average surface potential in which tangential field produced by the patches has negligible effects. This may not be true for emission type experiments. For introduction of the average CPD concept one also needs to assume that rule of additivity of surface potentials of individual adsorbed species applies, provided that depolarization of neighbouring dipoles is comperatively small and surface complexes are not formed. So, at least as the first order approximation, the average CPD is calculated from the surface potential contributions and amounts of individual adsorbates.

$$CPD = C_{Ni}\,\Theta_f + C_h\,\Theta_h + C_o\,\Theta_o + C\,\Theta_{ox} \tag{1}$$

Here Θ_f, Θ_h, Θ_o, and Θ_{ox} are fractional coverages of clean nickel, chemisorbed H_2, chemisorbed O_2, and nicked oxide, respectively. C_{Ni}, C_h, C_o are the surface potential contributions of clean nickel, and chemisorbed H_2 and O_2 at full coverage. C is the contribution due to nickel oxide on top of which are adsorbed H_2 and O_2. The surface potential of clean nickel was measured after desorption of H_2 in Ar atmosphere and was found to be $C_{Ni} = —0.074$ V[20,21]. The change of the CPD upon H_2 chemisorption reported in literature varies from —0.1 to —0.5 V depending on crystal surface and experiment.[20,21,25,26] I. Ogawa et al[26] measured H_2 and O_2 surface potentials by Kelvin's method and reported —0.4 V and —0.55 V, respectively. Their result for H_2 is close to —0.35 V found in this work (shown on the Figure 2.). Since the CPD of O_2 could not be measured in this work, because under the experimental conditions chemisorption occurs with simultaneous oxidation[20,21], the value from the work of I. Ogawa $C_o = —0.55$ V was taken.[26] The CPD contribution of the oxidized surface with adsorbed H_2 and O_2, was measured in the range of pO_2 (1—10 kPa), where the oscillations disappear, and the CPD attains almost the constant value $C = —0.025$ V[20,21], also shown on the Figure 2. The rate of H_2 chemisorption and desorption is determined from

$$r_H = k_1\,\Theta_f{}^2\,[pH_2] - k_{-1}\,\Theta_h^2 \qquad K_1 = k_1/k_{-1} \tag{2}$$

where pH_2 is the partial pressure of H_2, and k_1 and k_{-1} are rate constants, and K_1 is the adsorption equilibrium constant. The rate of O_2 chemisorption is determined from impingement rate of O_2 molecules upon the surface, assuming that initial sticking coefficient $s_o = 1$.[27,28] Initially, every molecule that hits the surface sticks to it and is disociatively chemisorbed on adjacent atoms. It follows from the kinetic theory of gases

$$r_o = (2\pi\, \mathrm{m}\, k_B\, T)^{-1/2}\,\Theta_f^2\,[pO_2] \tag{3}$$

pO_2 is the O_2 partial pressure, m is the molecular weight, and T is the reactor temperature. Additionaly, it is assumed that H_2 and O_2 dissociatively adsorb and desorb on the oxide. The rates are governed by the following equations

$$\overline{r_h} = k_6\,\Theta_f^2\,[pH_2] - k_{-6}\cdot\overline{\Theta}_h{}^2 \qquad k_6 = k_6/k_{-6} \tag{4}$$

$$\overline{r_O} = k_7\,\overline{\Theta}_f{}^2\,[pO_2] - k_{-7}\,\overline{\Theta}_o{}^2 \qquad K_7 = k_7/k_{-7} \tag{5}$$

$\overline{\Theta}_h$, and $\overline{\Theta}_o$ are the fractional coverages of chemisorbed H_2 and O_2 on the oxide, and $\overline{\Theta}_f$ is the surface coverage of the vacant sites on the oxide. The initial oxidation of the surface is believed to occur through the exchange mechanism of chemisorbed oxygen with underlaying nickel atoms.[29] The initial rate can be expressed as $k_2\,\Theta_o{}^n$, where n is approximately the number of O_2 atoms, formed in a cluster, required to provide sufficient potential to pull a nickel atom from the crystal structure and to start the oxidation process. Further oxidation proceeds through interaction of adsorbed O_2 atoms over the sites where the exchange mechanism started. Hence, the total rate of oxidation is given by

$$r_{OX} = k_2\,\Theta_o{}^n + k_3\,\overline{\Theta}_o{}^a\,\overline{\Theta}_{ox}{}^b \tag{6}$$

k_2 and k_3 are specific rate constants, a, b are parameters. The oxide is reduced from hydrogen atoms adsorbed on top of the oxide and from H_2 present on the reduced fraction of the surface. The autocatalytic effect of the reduced metal has been observed form the earliest rate measurements,[12] the CPD measurements,[20] and by the LEED experiments.[30] The rate of the reduction is expressed in the form

$$r_{RD} = k_4 \Theta_h^{\,c} \Theta_{ox}^{\,d} + k_5 \bar{\Theta}_h^{\,e} \Theta_{ox}^{\,f} \tag{7}$$

k_4, k_5 are specific rate constants, while c, d, e, f are constant parameters. From the data on the Figure 5. it is evident that the reduced as well as the oxidized nickel surface catalyse the oxidation of H_2, therefore the both rates need to be taken into account. The rate of H_2O production over the reduced fraction of the surface is

$$r = k\, \Theta_h^{\,2}\, \Theta_o \tag{8}$$

and the rate over the oxidized fraction is

$$\bar{r} = \bar{k}\, \bar{\Theta}_h^{\,2}\, \bar{\Theta}_o \tag{9}$$

k and $\bar{k}$ are specific rate constants. The total rate of H_2O production is the sum of (8) and (9) plus the rate of H_2O produced from reduction of the oxide (1O)

$$r_{H_2O} = r + \bar{r} + r_{rd} \tag{10}$$

Balance of the sites on the surface is given by

$$\Theta_f + \Theta_h + \Theta_o + \Theta_{ox} = 1 \tag{11}$$

while the balance of the sites over the oxidized fraction is

$$\bar{\Theta}_f + \bar{\Theta}_h + \bar{\Theta}_o = \Theta_{ox} \tag{12}$$

For a mathematical model to predict the limit cycle behaviour at least two dynamical variables need to be defined. From the CPD measurements Ž. Kurtanjek et al.[20–24] deduced that oscillations are due to transition from chemisorbed oxygen, on a mainly reduced surface, to a partly oxidized surface. Therefore the process is modeled by the balance equations for Θ_o and Θ_{ox} as the rate determing steps.

$$N_o \frac{d\,\Theta_o}{d\,t} = A\,(2\,r_o - r - r_{ox}) \tag{13}$$

$$N_o \frac{d\,\Theta_{ox}}{d\,t} = A\,(r_{ox} - r_{rd}) \tag{14}$$

The balance is based in number of O_2 atoms present on the surface. N_o is the number of active sites, A is the total area. Dynamical changes of all the species and the reaction rates are governed by the equations (13) and (14). The fractional coverages of H_2 on the reduced fraction of the surface and on the nickel oxide, as well as the coverage of O_2 on the oxide, are assumed to establish fast eqilibrium with respective partial pressures in the gas phase. These assumptions lead to the following set of equations

$$\Theta_{\mathrm{h}} = \Theta_{\mathrm{f}} \sqrt{K_1 [p\mathrm{H}_2]} \tag{15}$$

$$\Theta_{\mathrm{h}} = \Theta_{\mathrm{f}} \sqrt{K_6 [p\mathrm{H}_2]} \tag{16}$$

$$\Theta_{\mathrm{o}} = \Theta_{\mathrm{f}} \sqrt{K_7 [p\mathrm{O}_2]} \tag{17}$$

When the equations (15), (16), (17) are combined together with the equations for the balance of the coverages (11) and (12) one obtaines the relationship between Θ_{o}, Θ_{ox} and the rest of the variables. Hence, the model is reduced to the two nonlinear differential equations (13) and (14) in two variables Θ_{o}, Θ_{ox}. The complete model equations are given in the Appendix. Analysis of the model consists in an examination of steady state solutions and eigenvalues of the linearized system combined with numerical solutions of steady states and computer simulation of transients and limit cycles. Expansion of the equations around the steady state and neglecting higher derivatives leads to the linearized system

$$\frac{\mathrm{d}}{\mathrm{d}\,\tau} \begin{pmatrix} \Theta_{\mathrm{o}} \\ \Theta_{\mathrm{ox}} \end{pmatrix} = \begin{pmatrix} J_{11} & J_{12} \\ J_{21} & J_{22} \end{pmatrix} \begin{pmatrix} \Theta_{\mathrm{o}} \\ \Theta_{\mathrm{ox}} \end{pmatrix} \tag{18}$$

$$\tau = t\,A/\mathrm{N} \qquad tr\ J = J_{11} + J_{22}$$

$$det\ J = J_{11}\,J_{22} - J_{12}\,J_{21}$$

where J_{ij} is the Jacobian matrix. According to theory of stability[1] if $tr\ J$ changes its sign from minus to plus, while $det\ J$ remains positive, the steady state becomes unstable. If a steady state is unique and unstable, than it is surrounded by a limit cycle. Unfortunately, it is not a sufficient condition for equations to produce a stable periodic output. An unstable steady state may be surrounded by an unstable limit cycle, which in turn may be surrounded by another one, etc. Therefore, to predict oscillatory behaviour, one needs to examine the properties at the large, which is only possible by examing the solution space by computer simulation of nonlinear differential equations. In this work attention was focused on the changes of the stability properties of the steady states as a function of $p\mathrm{O}_2$ and subsequent computer simulation. It can be shown, by inspecting the signs of the partial derivatives, that if the following condition is satisfied

$$\frac{\partial}{\partial\,\Theta_{\mathrm{ox}}} \begin{pmatrix} \text{rate of} \\ \text{reduction} \end{pmatrix} > \frac{\partial}{\partial\,\Theta_{\mathrm{ox}}} \begin{pmatrix} \text{rate of} \\ \text{oxidation} \end{pmatrix} \tag{19}$$

all the steady states are unique and stable. Violation of (19) is then a necessary condition for the existence of an oscillatory solution. Because the model contains seventeen unspecified parameters, a systematic investigation of the dynamical properties of the system in the complete parameter space is out of hand. The parameters were determined by a trial and error method until the equations predicted bifurcation points in agreement with the experimental data shown in Figure 2. (Values of the parameters are given in the Appendix). The oscillations appear at $p\mathrm{O}_2 \approx 100$ Pa and disappear at $p\mathrm{O}_2 \approx 1$ kPa, while the model predicts the bifurcation points at $p\mathrm{O}_2 = 220$ Pa and $p\mathrm{O}_2 = 850$ Pa. Marquardt's[31] algorithm was used to calculate steady states, and by using

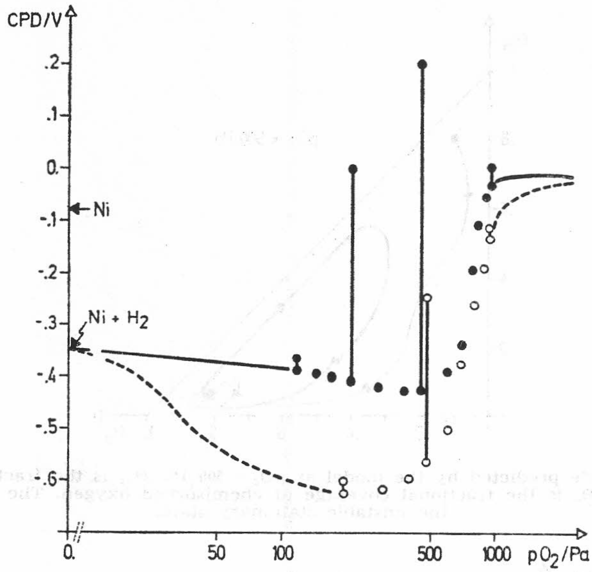

Figure 2. CPD variations as function of partial pressure of oxygen pO_2 at gas velocity 0.064 m/s, $T = 543$ K. The solid line are experimentaly observed steady states, and the broken line are the model predictions. With circles are denoted oscillatory states and maximum amplitudes.

different initial conditions they were checked for uniqueness. For simulation of transients and limit cycles M. L. Michelsen's[32] integration routine for stiff systems was used. In Figure 3. the results of a simulation for $pO_2 = 500$ Pa are shown. There is an unique unstable steady state surrounded by a limit cycle. In the same manner other oscillatory states were checked. The corresponding changes of the CPD were calculated by means of equation (1). Figure 2. shows the calculated CPD values in the stable regions, before the first and after the second bifurcation point, as well as average CPD values in the oscillatory region. The model predicts that at low pO_2 (below 220 Pa) the surface is mainly covered with chemisorbed O_2 and H_2, increase of pO_2 produces increase of chemisorbed O_2 coverage, and at maximum ($\Theta_o = 0.85$) a bifurcation to an oscillatory state occurs. At the samo point, the fractional coverage of nickel oxide is negligible $\Theta_{ox} < 10^{-4}$. Further increase of pO_2 decreases the coverage of O_2 at the expense of the oxide. In the oscillatory region the surface undergoes periodic oxidation and reduction. At the second bifurcation point the surface is mainly covered with the oxide, so for $pO_2 = 1$ kPa, $\Theta_{ox} = 0.82$, and reduced nickel is mainly covered with H_2, $\Theta_h = 0.13$. Beyond that point there is no significant change in the oxide coverage (at $pO_2 = 1.5$ kPa, $\Theta_{ox} = 0.89$). In Figure 4. the simulated CPD oscillations near the bifurcations are shown, $pO_2 = 300$ Pa and $pO_2 = 800$ Pa, and in the middle of the oscillatory region for $pO_2 = 500$ Pa. The first as well as the second bifurcation is soft. They appear as relaxation type oscillations, and disappear as a sine wave. Through the stable and oscillatory regions the steady and the average reaction rates of H_2O production were calculated. The results are shown in Figure 5. The model predicts correctly a bell type reaction curve

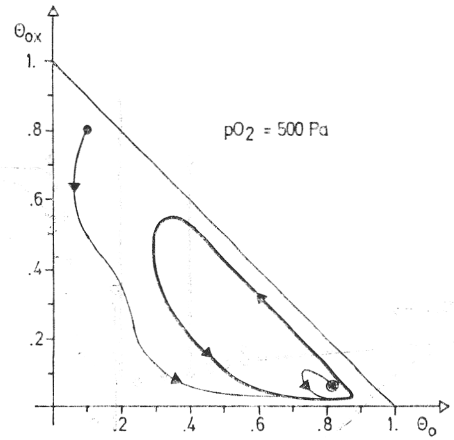

Figure 3. Limit cycle predicted by the model at $pO_2 = 500$ Pa. Θ_{ox} is the fractional coverage of nickel oxide, and Θ_0 is the fractional coverage of chemisorbed oxygen. The enclosed circle is the unstable stationary state.

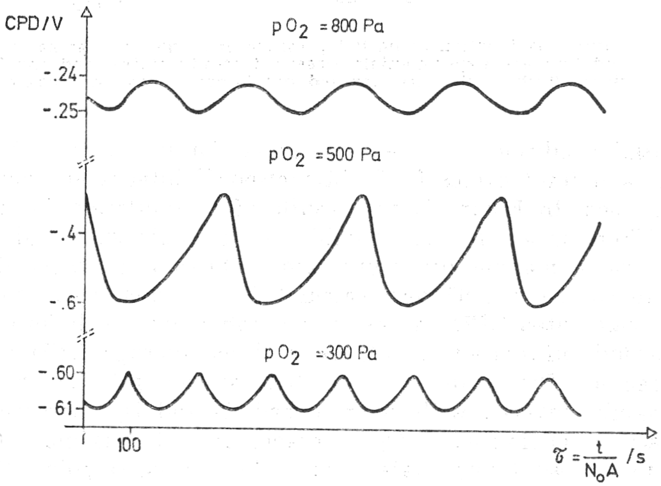

Figure 4. Computer simulation of CPD oscillations near the bifurcation points and in the middle of the oscillatory region.

with a maximum close to the second bifurcation point. The contribution of the reaction rates over the reduced nickel and the oxide are the left and the right lower activity branches, while the maximum is caused by the reduction of the oxide in the oscillatory region. If one compares the model simulations with the observed oscillations controlled by the surface reaction (the Figure 1c, 1d), one may conclude that the model fails. The conclusion is expected, since it is known that for simulation of chaotic behaviour more than two nonlinear differential equations are required. The results shown in the Figures 1a. and 1b. should be interpreted in terms of additional time constant introduced by mass and heat transfer resistance due to lower gas velocity, which

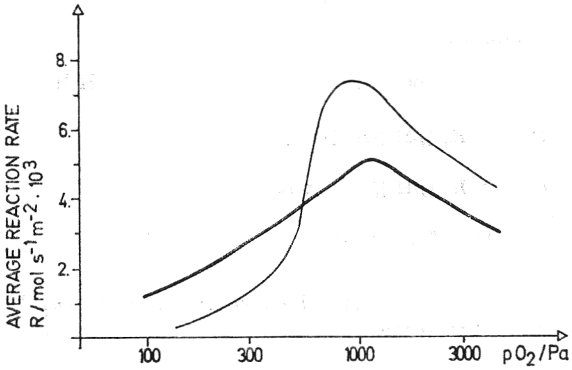

Figure 5. Average reaction rate of H_2O production as function of oxygen partial pressure. The thick line are the measured rates while the thin line are the rates predicted by the model.

has not been included in the model. Another obvious discrepancy is the difference between the maximum CPD amplitudes (the Figure 2.) and the model predictions. Most likely, the difference is caused by appearance of positive nickel ions on the surface during the course of the exchange mechanism, hence the high peaks toward the more positive surface potentials. Their contribution could not be included in the model due to lack of information on the dynamics of the mechanism and data on surface potentials of nickel ions. The most intriguing question addresses the problem of synchronization of the oscillatory concentration waves on the surface. The surface may be pictured as a collection of a large number of small domains. Each domain undergoes through a periodic oxidation and reduction behaving like an independent oscillator communicating with its surroundings. If there were no synchronization, a macroscopic observation due to averaging effects would not produce coherent collective behaviour because of phase differences of local oscillators. Bearing in mind the mechanism of synchronization it becomes clear that pseudo homogeneous models, like the one presented here, can not trully account for the dynamical behaviour. Hopefully models of the type proposed by M. Sheintuch and L. M. Pismen[33] will in future bring more light into the problem.

CONCLUSIONS

A mathematical model is proposed for the oscillatory oxidation rate of H_2 on nickel catalyst. The model consists of two nonlinear differential equations in the fractional coverages of chemisorbed O_2 and nickel oxide. The model predicts bifurcation points at $pO_2 = 220$ Pa and $pO_2 = 850$ Pa. Transition from a steady state to oscillatory state occurs at maximum surface coverage of chemisorbed O_2. The oscillations disappear when the surface is mostly covered with the oxide. A model is proposed for calculating average CPD changes as a function of the surface composition. The model predictions are compared with the experimental data and are found to be in semiquantitative agreement.

APPENDIX

The model equations are:

$$C_1 = \sqrt{K_7\,[pO_2]}/(1 + \sqrt{K_7\,[pO_2]} + \sqrt{K_6\,[pH_2]})$$

$$C_2 = \sqrt{K_6\,[pH_2]/K_7\,[pO_2]} \cdot C_1$$

$$C_3 = \sqrt{K_1\,[pH_2]}/(1 + \sqrt{K_1\,[pH_2]})$$

$$\mathrm{z} = (1 - \Theta_\mathrm{o} - \Theta_\mathrm{ox})$$

$$\frac{\mathrm{d}\,\Theta_\mathrm{o}}{\mathrm{d}\,\tau} = \frac{2\,(2\pi\,\mathrm{m}\,k_\mathrm{B}\,T)^{-1/2}}{(1 + \sqrt{K_1\,[pH_2]})}\,(1 - k\,C_3^2\,\Theta_\mathrm{o})\mathrm{z}^2 - k_2\,\Theta_\mathrm{o}{}^\mathrm{n} - k_3\,C_1{}^\mathrm{a}\,\Theta_\mathrm{ox}^{\mathrm{a+b}}$$

$$\frac{\mathrm{d}\,\Theta_\mathrm{xo}}{\mathrm{d}\,\tau} = k_2\,\Theta_\mathrm{o}{}^\mathrm{n} + k_3\,C_1{}^\mathrm{a}\,\Theta_\mathrm{ox}^{\mathrm{a+b}} - k_4\,C_3{}^\mathrm{c}\,\mathrm{z}^\mathrm{c}\,\Theta_\mathrm{ox}{}^\mathrm{d} - k_5\,C_2{}^\mathrm{e}\,\Theta_\mathrm{ox}^{\mathrm{e+f}}$$

Values of the model parameters are:

$[pO_2] + [pH_2] = 0{,}1$ MPa $T = 543$ K
$\mathrm{n} = 4$ $K_1 = 7 \cdot 10^{-4}$ Pa^{-1} $K_6 = 1$ Pa^{-1} $K_7 = 10^3$ Pa^{-1}
$k = 8 \cdot 10^{-2}$ mol m^{-2} s^{-1} $k = 7 \cdot 10^{-2}$ mol m^{-2} s^{-1} $k_2 = 4 \cdot 10^{-3}$ mol m^{-2} s^{-1}
$k_3 = 1.8$ mol m^{-2} s^{-1} $k_4 = 1.85$ mol m^{-2} s^{-1} $k_5 = 0.686$ mol m^{-2} s^{-1}
$\mathrm{a} = 0.2$ $\mathrm{b} = 0.2$ $\mathrm{c} = 2.5$ $\mathrm{d} = 0.1$ $\mathrm{e} = 3$ $\mathrm{f} = 0.1$

REFERENCES

1. M. Sheintuch and R. A. Schmitz, *Cat. Rev. Sci. Eng.* **15** 1 (1977) 107.
2. K. F. Jensen and W. H. Ray, *Chem. Eng. Sci.* **35** (1980) 2439.
3. V. D. Belyaev, M. M. Slinko, M. G. Slinko, and V. I. Timoshenko, *Kinet. Katal.* **14** (1973) 810.
4. V. D. Belyaev, M. M. Slinko, M. G. Slinko, and V. I. Timoshenko, *Doklady Physc. Chem., Akad. Nauk SSSR,* **214** (1974) 1098.
5. V. D. Belyaev, M. M. Slinko, and M. G. Slinko, *Proc. Sixth Inter. Congress Catal.,* London 1976, preprint B-15.
6. M. G. Slinko and M. M. Slinko, *Cat. Rev. Sci. Eng.* **17** (1978) 119.
7. C. A. Pikios and D. Luss, *Chem. Eng. Sci.,* **32** (1979) 191.
8. E. A. Ivanov, G. A. Chumakov, M. G. Slinko, D. D. Bruns, and D. Luss, *Chem. Eng. Sci.* **35** (1980) 795.
9. G. Eigenberger, *Chem. Eng. Sci.,* **33** (1978) 1225.
10. G. Eigenberger, *Chem. Eng. Sci.,* **33** (1978) 1263.
11. C. G. Takoudis, L. D. Schmidt, and R. Aris, *Chem. Eng. Sci.,* **37,** 1 (1982) 69.
12. A. T. Larson and F. E. Smith, *J. Amer. Chem. Soc.* **47** (1925) 347.
13. M. Boudart, F. V. Hanson, and B. Beegle, AIChE meeting, Chicago 1977.
14. R. A. Schmitz, G. T. Renola, and A. P. Zioudas, *Int. Congress on Kinetics of Physicochemical Oscillations,* Aachen 1979.
15. R. A. Schmitz, G. T. Renola, and P. C. Garrigan, *Conference on Bifurcation Theory and Applications in Scientific Disciplines, New York Academy of Science* (1977) paper no. 17.
16. C. G. Vayenas, C. Georgakis, J. Michaels, and J. Tormo, *J. Catalysis* **67** (1981) 348.
17. C. G. Vayenas, B. Lee, and J. Michaelis, *J. Catalysis* **66** (1980) 36.
18. K. F. Jensen and W. H. Ray, *Int. Congress on Physicochemical Oscillations,* Aachen 1979.
19. K. F. Jensen and W. H. Ray, *Chem. Eng. Science* **35** (1980) 241.

20. Ž. Kurtanjek, *Ph. D. Dissertation*, The University of Houston, 1979.
21. Ž. Kurtanjek, M. Sheintuch, and D. Luss, *J. Catalysis* **66** (1980) 11.
22. Ž. Kurtanjek, M. Sheintuch, and D. Luss, *Proc. Conf. Kinetics of Physichemical Oscillations*, Aachen (1979) 191.
23. Ž. Kurtanjek, M. Sheintuch, and D. Luss, *Ber. Bunsenges. Phys. Chem.* **84** (1980) 374.
24. Ž. Kurtanjek, *2nd Yugoslav-Italien-Austrian Chem. Eng. Conf.*, Bled (1980) 396.
25. R. V. Culver and F. C. Tompkins, *Advances in Catalysis* **11** (1959) 67.
26. I. Ogawa, T. Doke, and I. Nakada, *J. Appl. Physc. (Japan)* **21** (1952) 223.
27. P. H. Holloway and J. B. Hudson, *Surf. Sci.*, **43** (1974) 123.
28. P. H. Holloway and J. B. Hudson, *Surf. Sci.*, **43** (1974) 140.
29. F. P. Fehlner and N. F. Mott, *Oxidation of Metals*, **2**, 1 (1970) 59.
30. J. W. May and L. H. Germer, *Int. Mat. Sci. Conference, Berkley* 1968, p. 51—3.
31. D. W. Marquardt, *J. Soc. Appl. Math.*, **11** (1963) 431.
32. M. L. Michelsen, *AIChE J.*, **22**, 3 (1976) 594.
33. M. Sheintuch and L. M. Pismen, *Chem. Eng. Sci.*, **36** (1981) 489.

SAŽETAK

Oscilatorna stanja pri oksidaciji vodika na niklu

Željko Kurtanjek

Istraživanja su oscilatorna stanja u reakciji oksidacije vodika na niklu mjerenjem CPD. Oscilacije su nađene u temperaturnom području 433—673 K za brzine plinova 0,006—2,5 m/s. Pri brzinama iznad 0,1 m/s oscilacije u temperaturi katalizatora i sastava plinova su nestale, upućujući na zaključak da su oscilacije prouzrokovane kemijskom reakcijom na površini. Predložen je matematički model izveden pod pretpostavkom da dolazi do istovremene oksidacije i redukcije površine. Taj model predviđa oscilatorna stanja i semikvantitativno se slaže s eksperimentalnim podacima.