The Kinetics of Catalytic Reactions Studied by Resistivity Measurements on Thin Metal Films

H.-U. Finzel[a], Bi Heping[b], and P. Wissmann[c]

[a] Fachhochschule Niederrhein, FB Physikalische Chemie, Adlerstr. 32, D-47998 Krefeld
[b] On leave from Yuci University, PR China
[c] Institut für Physikalische Chemie der Universität Erlangen-Nürnberg

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Resistivity measurements on thin films are very suitable for the study of the kinetics of reactions on metallic surfaces. The oxidation of carbon monoxide on palladium is investigated as an example of great technical relevance, where details of the reaction mechanism and the film structure are well-known from literature. The time dependence of the change in resistivity is quantitatively interpreted with the help of a diffusion model based on a Monte-Carlo simulation of the gas coverage of the surface.

Key words: Heterogeneous Catalysis, Kinetics, Resistivity, Thin Metal Films.

1. Introduction

A resistivity increase is usually observed during gas adsorption on thin metal films [1 - 2]. The increase amounts to about 3 % in the case of CO adsorption on 30 nm thick Pd films [3]. Complications arise, however, if oxygen is coadsorbed at ambient temperature. Then, the adsorbed carbon monoxide is oxidized according to [4, 5]

$$CO + O \rightarrow CO_2. \qquad (1)$$

The adsorption [6 - 9] and oxidation [9 - 11] of carbon monoxide on Palladium surfaces has intensively been studied by many groups because of the use of Pd in technical catalysis, for example in automobile exhaust decontamination. The CO is molecularly adsorbed with the molecule axis perpendicular to the Pd surface, the oxygen on the vacuum side. In order to obtain defined surface conditions, often single-crystals of Pd serve as catalysts, and modern ultrahigh-vacuum techniques and spectroscopies are used to prepare the surfaces, to control the cleaning procedure, and to characterize the reaction progress. All authors state that a dissociation of molecular oxygen is a necessary precondition for the CO_2 formation, i. e. the reaction follows a Langmuir-Hinshelwood mechanism [11]. Such a dissociation occurs for all orientations of the Pd surfaces under room temperature conditions, details having extensively been described in the literature [4, 5, 9, 12]. For sufficiently small CO coverages, it is assumed that the adsorbed CO diffuses much more quickly than oxygen on the surface, so that the CO diffusion is rate determining in the reaction [4]. For higher precoverages, the adsorbed CO forms domains, and the interaction with oxygen is only effective at the domain boundaries. The reaction only proceeds, however, if the degree of CO coverage θ does not exceed a critical value ($\theta = 1/3$ [4], which roughly corresponds to $n = 8 \cdot 10^{14}$ molecules/cm^2 for our films, taking into account the still present roughness of the surface). The CO mobility is drastically reduced by the domain formation, and the diffusion of the dissociated oxygen atoms is now likely to be the rate determining step.

The main aim of the present paper is to show that resistivity measurements are a very suitable tool to study the reaction kinetics. On one hand, the adsorption of CO and O_2 leads to a distinct increase in resistivity as mentioned above. On the other hand, CO_2 is formed according to (1) and immediately desorbs after formation. Hence, a net decrease in resistivity is observed during the progress of the reaction. In order to enable a quantitative evaluation, we have developed a theory which allows the extraction of kinetic data from the measured time dependence of the resistivity. The applicability of the theory is checked with

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Reprint requests to Prof. Dr. H.-U. Finzel.

experimental data obtained for about 20 nm thick Pd films deposited on glass.

2. Experimental

An experimental set-up of high detection sensitivity for the resistivity has been described in detail in [1]. In order to guarantee conditions comparable to previous work [3], we have deposited the palladium films on glass substrates at ambient temperature, and annealed them at 100 °C for 1 h to stabilize the structure. The gas was dosed at ambient temperature or at 77 K, respectively, by breaking the seals of suitably dimensioned ampoules filled with chemically pure CO or O_2. The thickness of the Pd films was estimated from the resistivity measured in situ during the film deposition, and was finally determined after completion of the experiments by dissolving the films and performing atomic absorption spectroscopy. The error of the thickness determination was estimated to be 5 % maximum.

The structure of the films is homogeneous but polycrystalline, as described in [13]. The films show a preferred (111) orientation but no azimuthal alignment of the crystallites. Hence a single-crystalline Pd(111) surface seems to be the best theoretical approximation for the description of the real surface while neglecting roughness phenomena. The resistivities measured for the pure films agree with data published by Wedler and Alshorachi [14].

3. Results

In [3] it was shown that the expected increase in resistivity $\Delta\rho$ during CO adsorption occured in all cases and at all temperatures (i. e. for 77 K and ambient temperature). The initial linear dependence on CO coverage n at small coverages obeyed the relation

$$\left(\frac{\partial\Delta\rho}{\partial n}\right)_{n\to 0} = \frac{A\rho_o l_o}{d}, \tag{2}$$

where A is the scattering cross section, d the film thickness, and $\rho_o l_o$ a measure of the free electron density ($A = 2.0$ Å^2; $d = 17$ nm; $\rho_o l_o = 11.3 \cdot 10^{-12}\Omega$ cm^2. Concerning problems related to the applicability of the free electron approximation to the case of Pd we refer to [3]). The temperature becomes important if oxygen is added to the surface. At 77 K, the resistivity is further increased by the oxygen. The shape of the resistivity versus coverage curve is parabolic [1, 15] in the whole coverage range investigated here as is shown in Fig. 1 (solid curve). No reaction takes place at this temperature, and the scattering cross sections for CO and O on Pd do not differ much.

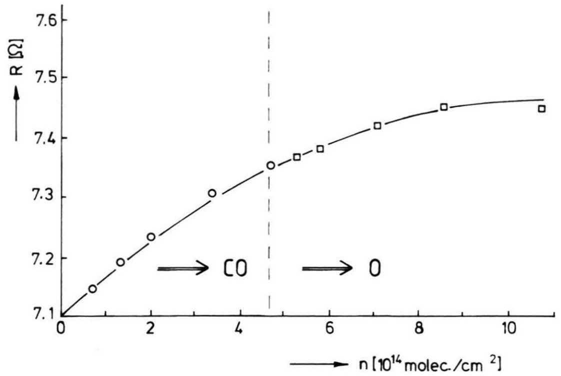

Fig. 1. Change in the resistivity of a 17 nm thick Pd film during CO adsorption (○) and subsequent O adsorption (□) at 77 K. The solid curve represents a parabola. n is the total gas coverage ($n = n_{CO} + n_O$).

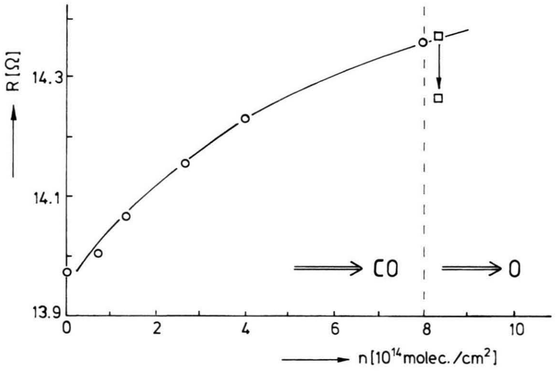

Fig. 2. Change in the resistivity of a 17 nm thick Pd film during CO adsorption (○) and subsequent O adsorption (□) at 293 K. The solid curve represents a parabola. n is the total gas coverage ($n = n_{CO} + n_O$). The arrow indicates that the resistivity decreases with time.

Now we will discuss the CO adsorption at 20 °C. In Fig. 2, we have plotted the resistivity observed 15 minutes after CO inlet where a more or less pronounced saturation is reached. The dependence of the resistivity on coverage is comparable to the case of 77 K. The only exception is the measuring point which is attributed to the oxygen dosage at 20°C (square in Fig. 2). Here, immediately after O_2 dosage a very quick increase of the resistivity occurs, followed by a slow decrease. No saturation could be achieved in

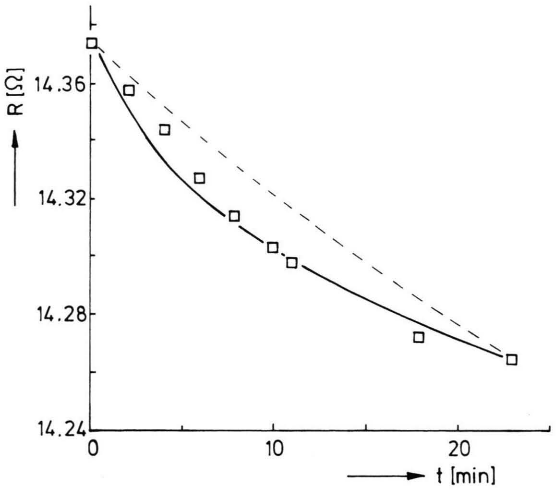

Fig. 3. Time dependence of the resistivity decrease after O_2 dosage at 293 K (refer to Fig. 2). Measured points (□) along with theoretical curves calculated for the second-order reaction (- - -) and for the diffusion model (—). The initial quick increase mentioned in the text occurs on a second scale and has been omitted in the figure for clarity reasons.

reasonable times, the resistivity steadily decreases as shown in Figure 3. Obviously, the oxygen first adsorbes at non-reactive sites where the dissociation of oxygen occurs. This is reflected by the initial resistivity increase. Then, the dissociated oxygen atoms diffuse to the boundaries of the CO domains where CO_2 is formed and immediately desorbed. Thus, the net gas coverage effective for the resistivity increase is reduced, and the resistivity decreases.

4. Theoretical Models

The simplest model to describe the kinetics of CO oxidation is a second-order reaction where the reaction velocity is proportional to the CO coverage at the surface as well as to the oxygen coverage [5, 16]. Such a model cannot take into account, however, that the CO molecules inside the domains do not participate in the reaction. Hence we have modified the description by simulating the gas distribution at the surface by Monte-Carlo methods assuming that the rate determining step is the surface diffusion of the oxygen [17 - 18]. In both models, a parabolic dependence of the resistivity on the net gas coverage is assumed. Note that the gas transport to the film surface [19] and the dissociation of oxygen [13] according to

$$O_2 \rightarrow 2\,O \tag{3}$$

are so quick that the resistivity kinetics remains unaffected by these phenomena.

4.1. *Second-order reaction*

First we will show that a simple second-order rate equation is no sufficient approximation to describe the measured time dependence of resistivity. Starting point for our calculation is the equation [16]

$$\frac{\partial n_{\mathrm{CO}}}{\partial t} = -k n_{\mathrm{CO}} n_{\mathrm{O}}, \tag{4}$$

where n_{CO} and n_{O} are the coverages of CO and O, respectively. The correlation with the resistivity increase $\Delta\rho$ is given by the parabolic law [1]

$$\frac{\Delta\rho}{\Delta\rho_{\max}} = \frac{n}{n_{\max}}\left(2 - \frac{n}{n_{\max}}\right). \tag{5}$$

Here we have implicitly assumed that the scattering cross sections of CO and O do not differ much, i. e. the effective coverage n is

$$n = n_{\mathrm{CO}} + n_{\mathrm{O}}. \tag{6}$$

$\Delta\rho_{\max}$ and $n_{\max}$ in (5) can be obtained from Fig. 2; only the rate constant k remains to be fitted. Figure 3 shows the optimum theoretical curve (dashed curve) fitted to the experimental values at $t = 0$ and $t = 23$ min. Evidently, the dashed curve does not agree with the measured values. Similar conclusions have been drawn by Engel and Ertl [5] from their kinetic studies. Note that the disagreement is even more pronounced when a pseudomonomolecular rate equation is used instead of (4).

4.2. *Diffusion model with Monte-Carlo simulation*

In order to achieve a better agreement between experiment and theory we have developed a model which takes into account the domain structure of the preadsorbed CO, the dissociation of the O_2 molecules adsorbed, and the migration of the oxygen atoms on the Pd(111) surface. As mentioned above, the CO domains are formed up to a coverage degree of $\theta = 1/3$, the diameter is about 30 nm [4]. We have assumed the domains to be circular with a fixed diameter but statistically distributed on the surface. O_2 is adsorbed on Pd bridge sites which are not occupied by the CO domains. The dissociation results in pairs of oxygen atoms adsorbed on two neighbouring but statistically distributed free bridge positions [4]. Subsequently the O atoms can migrate in six directions ($6 \cdot 60° = 360°$) due to the sixfold symmetry of the Pd(111) surface [20]. If a new bridge site is reached, the site-to-site hopping starts again. The interaction with other oxygen atoms adsorbed is included in the calculation in so far as the program asks whether the neighbouring bridge site is occupied by another oxygen atom or not. If the neighbouring site is free, the diffusion proceeds. If it is occupied, the jump of the oxygen atom is cancelled. The recombination of oxygen atoms and desorption of molecular oxygen are totally excluded in these considerations.

The migration of the oxygen atoms proceeds until they meet the boundary of a CO domain which is assumed to remain fixed. Then, the formation of CO_2 and immediate desorption is postulated. The reaction leads to a decrease of the diameter of the CO domains and thus to a reduction of resistivity according to (5). The result obtained on the basis of such a diffusion model is shown in Fig. 3 (solid curve). Again the theoretical curve is fitted to the experimental points at $t = 0$ and $t = 23$ min, respectively. The agreement is much better than for the second-order reaction.

From the fit in Fig. 3 we obtain the mean time necessary for a diffusion from one bridge site to another. Hence we can estimate the diffusion coefficient D on the basis of a random-walk picture [16] in spite of the fact that the mutual interaction of the oxygen atoms is not totally neglected in our model. Using

$$x^2 = 4Dt \tag{7}$$

and the well-known spatial separation x of two bridge positions for a Pd(111) surface we obtain $D = 2.7 \cdot 10^{-16}$ cm^2/s. Note, that this D value should, strictly spoken, still depend on time due to the mutual interaction of the oxygen atoms mentioned above.

We expect even smaller D values for the motion of the CO clusters. On the other hand, von Oertzen et al. have evaluated PEEM micrographs [21] of diffusing CO molecules on well-ordered Pd(111) surfaces cleaned by laser-induced thermal desorption, and have reported D values as high as $D \approx 10^{-7}$ cm^2/s. This discrepancy may be attributed to the surface roughness still effective for our films which reduces the CO mobility. Generally, one should be very cautious in comparing D values obtained with different techniques. A typical example in this context is the CO/Pt(111) system. The D values published by various groups differ by more than four orders of magnitude [22 - 24]. Possible reasons for this are manyfold: (a) the underlying of too rough assumptions in the evaluation procedure, (b) uncertainties in the coverage determination, and (c) undefined surface properties of the Pd catalyst used. Hence it is particularly desirable to develop new and independent methods of determination of D.

5. Conclusions

The analysis of the resistivity of thin metal films can lead to useful information on the kinetics of catalytic reactions. This is demonstrated for the example of CO oxidation on Pd films. A simple second-order reaction is a too rough approximation for a reliable description. It is shown, that a statistical model can be better adapted to the experimental realities. We postulate that large CO domains are formed on the Pd surface, and that oxygen diffuses to the CO domain boundaries where it reacts to CO_2 immediately desorbing. The film surface is represented in our model by a (111) oriented surface which may be a reasonable approximation in spite of the fact that our investigation deals with polycrystalline (111)-textured films which are not ideally smooth but exhibit a certain roughness in the surface. This roughness is probably responsible for the deviations between theory and experiment [25] still evident in Figure 3.

The diffusion coefficient of oxygen on the films is found to be $D = 2.7 \cdot 10^{-16}$ cm^2/s. Note that the model depends on the special coverage conditions. We have treated here rather high precoverages of CO. For very small precoverages, higher D values are expected which should be attributed to a diffusion of statistically adsorbed CO molecules towards the stronger bound oxygen atoms [21]. This case will be treated in a forthcoming paper [26]. Moreover, we plan refinements of the model like further specification of the mutual interaction of adsorbed oxygen atoms as well as of the possible influence of precursor states [27]. A quantitative evaluation of activation energies which are principally accessible by a variation of temperature [21, 28] seems to be problematic in the present case. It should be assured for such an evaluation that the CO remains undissociated at the surface even at higher temperatures [29].

Finally we should mention that the influence of roughness and plane specifity on the reaction mechanism becomes quite evident for the Pd(110) / CO + O system where oscillatory reaction rates have been reported in the literature [30, 31]. Such oscillations could never be established by resistivity measurements on polycrystalline Pd films to the best of our knowledge.

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