JOURNAL OF CATALYSIS **100**, 377–382 (1986)

Hydrogen Spillover and H–D Exchange in the System Pt/Al_2O_3

II. Experimental Problems and Influence of OH- or OD-Coverage

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Received November 20, 1985; revised March 20, 1986

In the first part of this investigation it was shown that, using strictly constant methods of preparation of the sample, reproducibility and precision of kinetic Fourier transform-infrared measurements are sufficient to obtain quantitative values for velocity constants for H–D exchange reactions of surface OH groups in the system Pt/Al_2O_3. The exchange reactions show a fast and a slow partial reaction, the relative abundance of which depends on the initial coverage of the oxide with OH or OD. Model calculations are based on the assumption that those hydroxyls which exchange in a fast reaction are those which are connected with a Pt crystallite via adjacent hydroxyl groups.

1. INTRODUCTION

Hydrogen spillover is the transfer of activated hydrogen species from a metal (Pt, Ni) to the surface of a carrier such as Al_2O_3 or SiO_2. This effect has been described by many authors, using different methods for the investigation. A review was given by Bond (*1*) in 1983. Khoobiar (*2*) and Levy and Boudard (*3*) observed the transformation of WO_3 to tungsten hydrogen bronze with a mixture of Pt/Al_2O_3 and WO_3. Bianchi *et al.* (*4, 5*) describe an increase of activity for hydrogenation reactions by oxides after treatment with spillover hydrogen, and the formation of methane from surface methoxyl groups with the activated hydrogen species (*6*). Kramer and Andre (*7*) detected adsorbed hydrogen by TPD at the same desorption temperature after spillover as after a treatment with hydrogen atoms produced in an electric discharge. Several authors used IR to investigate H–D exchange. Thus Eischens and Pliskin (*8*) first observed an increase in exchange velocity by the metal in the system Pt/SiO_2. Hall and Lutinski (*9*) as well as Bianchi *et al.* (*4*) were able to show that traces of water (oxygen) in the system leads to an increase in exchange velocity. This effect was discussed by Bianchi *et al.* (*10*) too. Starting from H–D exchange on pure alumina (*11–13*) we investigated spillover and H–D exchange in the system Pt/Al_2O_3 (*14*), using FTIR spectroscopic methods.

In this paper we will first discuss some more technical details, reproducibility, and possible influence of pressure at which the wafers were produced.

In the second part the dependence on varying OH or OD coverage of the carrier will be discussed.

2. EXPERIMENTAL

Samples of 1% Pt on γ-Al_2O_3 (Degussa, Type C) were prepared by impregnation with a solution of $(NH_3)_2\,Pt(NO_2)_2$ in 25% ammonia and subsequent drying. This material was prereduced in H_2/He and hydrolyzed in H_2O/He at 500 K (*14*) to clean the oxide surface from any traces of chlorine. Wafers of this material (ϕ = 22 mm, 5 to 20 mg/cm^2) were compressed at 78.5 or 235 MPa. After pretreating the wafer in the heating zone of the measuring cell (*15*) for 2 h at 800 K in helium, to obtain constant

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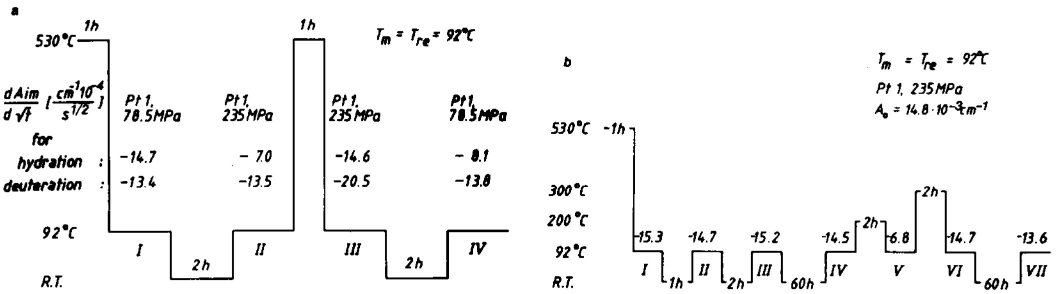

FIG. 1.(a) Reproducibility of reaction velocities and dependence on pressure at which the sample wafer was prepared. (b) Reproducibility of reaction velocities. Influence of conditions of pretreatment.

starting conditions, it was completely deuterated at the same temperature with D_2/He. After lowering the temperature the OD coverage was adjusted by injection of a mixture of O_2 and D_2 and heating at the so-called redeuteration temperature for half an hour. The H–D exchange was followed at 365 K using a reaction gas stream (50 ml/min) with 1.0×10^4 Pa H_2 in He. The gas streams had to be carefully purified from water and oxygen traces as described in (*14*). The reaction was followed using a Fourier transform–infrared spectrometer (Digilab FTS 14). Because of the better signal-to-noise value the bands of the surface OD groups on alumina were evaluated.

3. RESULTS AND DISCUSSION

3.1. Reproducibility

The reproducibility of the kinetic measurements depends on both the precision of quantitative measurements and the reproducibility of the exchange process itself. The results discussed here refer to the fast part of the reaction sequence (*14*). The velocity constants given (k) are of the form $dA_{im}/d\sqrt{t}$ (10^{-4} cm^{-1} s$^{-1/2}$), with A_{im} integral absorbance of a formal monolayer of the oxide surface (*16*). Figures 1a and b show k values for 15 measurements, obtained under slightly different conditions. From Fig. 1 it follows that the pressure at which the wafer was produced is without influence. Taking all k values, one obtains

$$k = (13.36 \pm 3.56) \times 10^{-4}\ \text{cm}^{-1}\ \text{s}^{-1/2}.$$

Figure 2, showing the distribution of k values, indicates that the distribution probably is not normal, but that the values below 10 and above 20 might be caused by bad experimental conditions. The lower values were indeed always obtained, if the samples remained at lower temperature for longer time, although this does not necessarily lead to wrong results, as two measurements show, where the samples were kept at room temperature for 60 h each before conducting the measurement. These observations led to the method of preparing the sample for the measurements described earlier. Under these conditions (discarding the four experiments mentioned) one gets

$$k = (14.36 \pm 0.68) \times 10^{-4}\ \text{cm}^{-1}\ \text{s}^{-1/2}$$

which means an error of about 5% for the determination of the k values. A compari-

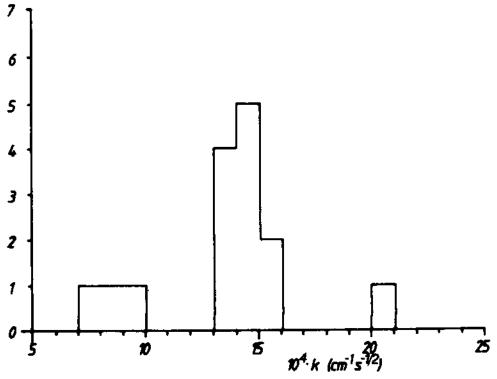

FIG. 2. Distribution of reaction velocity values.

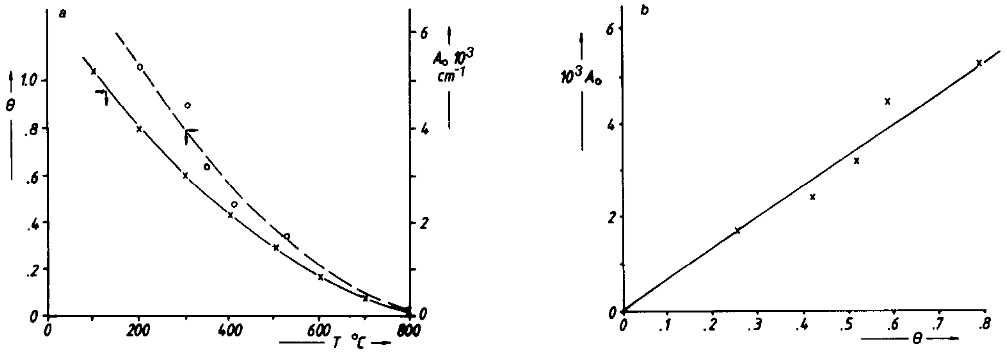

FIG. 3.(a) Temperature dependence of coverage (θ) after Peri (*17*) and of reduced initial absorbance A_0. (b) Relation between coverage (θ) and initial reduced absorbance A_0.

son of k values for hydrogenation and deuteration reactions leads to a kinetic isotopic factor of 1.04.

3.2. *Influence of OH and OD Coverage on Reactivity*

In order to determine the influence of the coverage it is necessary to have an unambiguous measure of coverage. The rehydration temperature is a nonlinear measure of this value (*17*), Fig. 3a, and it is necessary to work always under constant conditions, (e.g., time after rehydration). The initial absorbance of the OD band of a completely deuterated sample might lead to a linear relation with the coverage. For this purpose the absorbance may be reduced to the value of a formal monolayer of oxide

$$A_0 = \frac{A_i\,S_w}{m_w\,S_s}$$

A_i = initial, integral absorbance of OD band in the limits 2100 to 2800 cm^{-1};
S_w = cross section of wafer (3.80×10^{-4} m^2),
S_s = BET surface of alumina (100 m^2/g),
m_w = weight of wafer (g).

Figure 3a gives both the dependence of relative coverage (θ) after Peri (*17*) and of A_0 on temperature. Figure 3b shows the direct relation between A_0 and θ, leading to the approximate relation

$$\theta_{OD} = 150\,A_0$$

with about 2.32×10^{-5} mol OD/m^2 at $\theta = 1$.

In the investigation of the influence of coverage with OH and OD groups the same wafer was used always. It was redeuterated before each measurement to a different degree A_0 between 1.7×10^{-3} and 5.3×10^{-3} (corresponding to θ between 0.26 and 0.80). Figure 4a shows values of maximal absorbances as a function of time with the initial values indicated at the left side, and Fig. 4b gives the relative values (absorbance as percentage of initial value). The curves show that the former observation (*14*) of a fast and a slow reaction part are well reproduced. The figures further show that the amount of OD groups exchanged during the fast reaction clearly decreases with decreasing initial coverage with OD, leaving an increasing amount of OD groups, which may only be exchanged slowly. Curve V shows that—even under conditions of large θ values—a certain amount of OD groups seems not to react under the given conditions at all (~10%). As these bands were formed during the deuteration process at 803 K, there appeared to exist a strongly activated process which also permits an exchange of these OD groups.

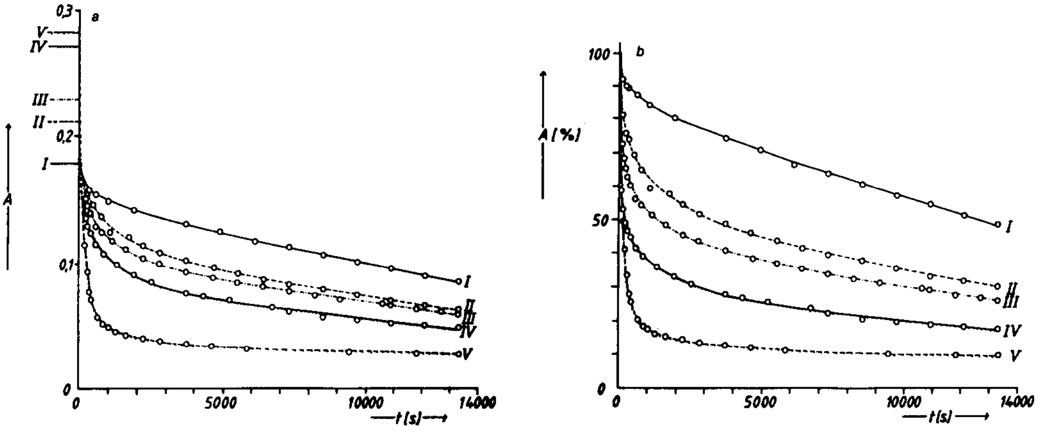

FIG. 4.(a) Exchange kinetics (maximal absorbances vs time) for samples of different initial coverage. (I) $T_{re} = 803$ K, $A_0 = 1.7 \times 10^{-3}$ cm^{-1}, $\theta = 0.26$; (II) $T_{re} = 673$ K, $A_0 = 2.4 \times 10^{-3}$ cm^{-1}, $\theta = 0.36$; (III) $T_{re} = 623$ K, $A_0 = 3.2 \times 10^{-3}$ cm^{-1}, $\theta = 0.48$; (IV) $T_{re} = 583$ K, $A_0 = 4.5 \times 10^{-3}$ cm^{-1}, $\theta = 0.68$; (V) $T_{re} = 478$ K, $A_0 = 5.3 \times 10^{-3}$ cm^{-1}, $\theta = 0.80$; (b) As (a) but with values relative to initial absorbance.

The existence of at least three partial processes prohibits a complete quantitative evaluation, but it shall be tried to give an interpretation of the general observations.

From other investigations (*18, 19*), we could show that the dissociative adsorption of hydrogen on the Pt crystallites is normally not the rate-determining step, as this step should strongly depend on hydrogen partial pressure. Even the transfer of hydrogen from platinum to the oxide surface may not be rate determining for the whole process, as the slowing down of the reaction and the different amount of OD groups reacting fast could not be explained. Thus the cause for the slowing down of the reaction must be a restricted transport depending on coverage with OH and OD groups.

The system under investigation consists of three phases: solid phase, gas phase, and surface phase. The transport of hydrogen species from the platinum crystallites to the ultimately exchangeable OD groups may take place via each of the three phases in principle. A transport through the solid phase should be a strongly activated process. Though no OH groups could be detected in the synthetic crystalline sapphire (α-alumina), it cannot be excluded that γ-alumina may contain hydroxyl groups, since silica contains similar nonreacting OH groups which are similar in structure with those of silica glass (*18*). These observations lead to the possible interpretation of those OH groups, which do not exchange at lower temperatures, as situated in the bulk of the oxide. The amount of the unreactive OH or OD groups cannot be determined exactly because their determination depends on the correct position of the baseline during the integration of the absorbance.

The second mechanism—transport through the gas phase—may only take place with reactive hydrogen compounds, as hydrogen atoms are thermodynamically too unstable. Under the given conditions only H_2O or HDO seem to be substances which may serve to transfer hydrogen to the OD groups. The exchange rate should depend on partial pressure of water, which is a function of coverage of the oxide with OH and OD. Thus the reaction should slow down with decreasing $\theta_{OH} + \theta_{OD}$, provided the exchange of D_2O with surface H on the Pt crystallites is not rate determining.

A slowing down of reaction velocity might occur under these conditions in cavities without Pt crystallites. But in contrast to the experimental results the relative

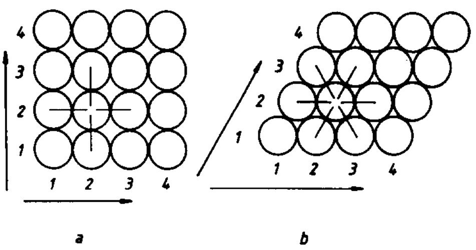

FIG. 5. Two idealized planes of alumina surface with representation of sites as matrix elements and next neighbors to one element. (a) (100)-plane; (b) (111)-plane.

amount of fast and slow exchanging deuteroxyl groups should be constant. This observation, together with the fact that the exchange of a wafer of pure oxide is not accelerated by a neighboring, Pt-containing sample, lead to the conclusion that this mechanism is not rate determining under the given conditions, which is in accord with the assumption in the literature cited before.

As a consequence the transport of hydrogen through the surface phase must be rate determining, at least during the slow reaction part. From the observations in Fig. 4 it follows that the transport easily takes place on a widely hydroxylized surface while it is hindered on the bare surface. This led to the following model: All those OD groups, which are connected to an exchange center (Pt) via adjacent OH or OD groups may exchange in a fast reaction. If there are "islands" of OD groups or single OD groups, which have no such direct contact, hydrogen must migrate over a bare oxide surface, which leads to a slow exchange of this part of OD groups.

The following stochastic model was used to calculate the relative abundance of fast and slow exchanging OD groups as a function of coverage with OH and OD groups (θ).

A matrix represents the sites on a (100)- or a (111)-plane of alumina. According to Fig. 5 the elements $(i - 1, j)$, $(i, j - 1)$, $(i, j + 1)$, and $(i + 1, j)$ represent neighboring sites on a (100)-plane; on a (111)-plane additionally the sites $(i - 1, j - 1)$ and $(i + 1, j + 1)$ are neighboring. In the beginning all the matrix elements are set equal to 1 (symbol for OH without neighboring OH groups). Using a random function, a certain number of elements is set at zero (dehydration). Thus the number of nonzero elements, relative to the total number of elements, is equal to θ. The next step is to test which of the sites are in contact with the exchange center(s). All those matrix elements are set equal to 2. The ratio of elements being 2 to those being 1 or 2 gives the relative abundance of rapidly exchangeable OD groups. After setting 1 all nonzero elements again the next dehydration step may take place. Since the border elements of the matrix would have a lesser chance of contact with the exchange center(s) because of the smaller number of neighbors, it was assumed that a border element may even exchange if a suitable element exists at the opposite border, i.e., the element (n, j) on a (111)-plane may exchange if either the element $(1, j)$ or $(1, j + 1)$ is 2.

The model was calculated with (a) only one element (1, 1) set equal to 2 (as a Pt particle) or (b) all those elements in line 1 set equal to 2 which were not equal O in each cycle, representing smaller or bigger Pt crystallites.

The calculations were made with 10*10 and 15*15 matrixes, 10 times each. More neighbors ((111)-plane) and "greater Pt

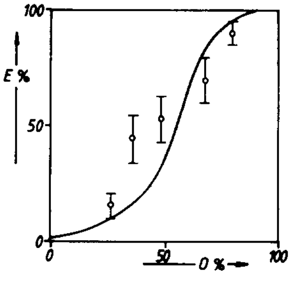

FIG. 6. Relative abundance of fast exchanging OD groups: experimental values from Fig. 4 (bars) compared with calculated values from model calculations (curve).

crystallites" shift the curve to the left side as expected. An averaged curve is shown in Fig. 6 together with experimental points obtained from Fig. 4. Since the evaluation of Fig. 4 is not very precise, the experimental results are given in form of bars. The topology of a real alumina surface is more complicated than that of the model and, moreover after Peri (*17*), the assumption of statistic dehydration is not strictly valid. Taking into account these limitations, the agreement between measurements and model calculations is fairly good.

4. CONCLUSIONS

Comparing these results with existing literature one may first consider the conformation of water (H_2O or D_2O) or OH or OD groups as necessary for the reaction (*2, 9, 19, 20*). In contrast to the previously cited literature, our measurements cannot be interpreted on the basis of transfer of hydrogen from the metal to the support as the rate-determining step for the whole reaction, which should be of first order under these circumstances. For samples with greater Pt loading or short transport distance on the oxide a rate limitation by phase transfer cannot be excluded, but for longer distances the transport is rate determining as concluded from (*14*), a conclusion which is also confirmed by Bianchi *et al.* (*10*) and by Conner *et al.* (*21*). A transport of spillover hydrogen into the bulk oxide, as observed by us at higher temperatures, was described by Sencier and Inami (*22*) and by Vannice and Neikam (*23, 24*) too. With respect to reaction velocity our values are about two orders of magnitude higher than that of Kramer and Andre (*7*) or of Bianchi *et al.* (*6*).

There are two possible explanations:

1. Two parallel reactions, one leading to H–D exchange and possibly to the formation of tungsten hydrogen bronze (*25*), both in a fast reaction, and the second forming reactive hydrogen on the oxide surface in a slow reaction.
2. The complete reaction may be a sequence with the formation of the reactive surface hydrogen in a slow consecutive reaction.

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