JOURNAL OF MATERIALS SCIENCE 24 (1989) 3691–3698

Kinetic–thermal processes of hydrogen sorption on Pd/WO_3 and Pd/MoO_3 bronze

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Kinetic–thermal investigations of the hydrogen sorption process in the temperature range from ambient to 720 K on powder samples of Pd/WO_3 and Pd/MoO_3 show that it takes place according to the "hydrogen spillover" mechanism, during which the corresponding hydrogen bronzes are formed. Hydrogen sorption changes the structure of the Pd/WO_3 bronze, while it breaks the structure of the Pd/MoO_3 bronze producing the amorphous state on heating to 570 K. The hydrogen bronze Pd/H_xWO_3, heated in oxygen, decomposes at around 830 K, resuming the original form of the yellow Pd/WO_3 bronze. A repeated cyclic heating of Pd/H_xMoO_3 bronze in hydrogen and oxygen in turn (thermogravimetric analysis and differential scanning calorimetry methods) shows that the sorbed hydrogen reacts violently with oxygen and to form water. In the opposite way, hydrogen sorption on the sample after heating in oxygen also proceeds violently, producing hydrogen bronze after the initial formation of water with oxygen. When heated in oxygen after hydrogen up to 720 K, the sample is oxidized to the maximum extent, returning to the original grey colour and the crystal state. Further heating in hydrogen produces a hydrogen bronze of dark blue colour, while the structure is decomposed. The kinetic processes were investigated and kinetic and thermal parameters were determined. The change in structure is also demonstrated by X-ray diffractometry and electron microscopy.

1. Introduction

Oxide bronzes constitute a particular and very important class of materials. The basic principle of their synthesis is the implantation of the electropositive element A into the oxide matrix of the MO_n oxide, where M is a transition metal (W, Mo, V) [1]. In place of the alkali metal A, hydrogen is fairly easily implanted into the oxide matrix, forming hydrogen bronzes H_xWO_3, H_xMoO_3, etc. [2, 3]. The valence of the transition metal is not changed in the process, as the alkali metal or hydrogen is "dissolved" in the oxide matrix in a non-stoichiometric ratio.

Synthesis of the bronzes is most frequently carried out according to standard methods, although new and more specific procedures have been published recently [4, 5]. In 1949 it had already been shown that at ordinary temperatures WO_3 reacts with atomic hydrogen obtained in a gas [6] or aqueous [7] phase, or through the "hydrogen spillover" process, forming tungsten bronze, H_xWO_3, which changes the yellow colour of WO_3 to blue. This colour change is used as a test for determining the presence of atomic hydrogen. The "hydrogen spillover" effect is the result of the reaction of the highly dispersed palladium and platinum on oxide materials with molecular hydrogen yielding atomic spilt-over hydrogen which spills from the surface of the metal and is sorbed by the oxide present or oxidized in an oxidizing medium, or involved in another reaction, depending on the medium. Among other workers, Sermon and Bond [8, 9] have particularly dealt with this problem in two extensive studies, presenting the results of other authors along with their own, investigating the spillover effect on various materials. It has been shown that in addition to the primary, a secondary hydrogen spillover process is also possible, i.e. the sorption on the support which does not contain platinum or palladium but is only in mechanical contact with either of them. Without going into details of the published data, it may be stressed that the significance of the hydrogen spillover process is great, as it enables atomic hydrogen generation, dehydrogenation of some organic compounds and also finds application in some catalytic processes.

Bearing in mind the presented and other published data, as well as the significance of the materials which take part in the hydrogen spillover process, attention in this work was focused mainly on investigating thermal, kinetic and structural parameters of the Pd/WO_3 and Pd/MoO_3 system with 0.1% Pd in flows of hydrogen, air, nitrogen and argon, at temperatures ranging from ambient to 720 K.

0022-2461/89 $03.00 + .12

2. Experimental procedure

Samples of Pd/WO_3 and Pd/MoO_3 were prepared in the usual way by impregnation of WO_3 and MoO_3 in an aqueous solution of $PdCl_2$, drying and heating for a few hours at raised temperatures until $PdCl_2$ was thermally decomposed. Hydrogen sorption on samples in the powder state prepared in this way was carried out under flowing hydrogen by differential scanning calorimetry (DSC) and thermogravimetry (TGA) on a DuPont 1090 Thermal Analyser. Structural investigations were carried out using a Philips PW-1051 diffractometer with Cu*Kα* radiation and a graphite monochromator.

3. Results and discussion

It was shown that both systems (Pd/WO_3 and Pd/MoO_3) sorb hydrogen exothermally, forming the corresponding hydrogen bronzes, in agreement with published data [6, 8, 9]. Exposure to air, argon or nitrogen results in desorption of hydrogen, with the colour of the hydrogen bronze remaining unchanged (dark blue). Repeated heating in hydrogen repeats the process of sorption.

Kinetics of the sorption process was investigated by the method of non-isothermal DSC analysis based on non-isothermal DTA analysis of chemical reactions in homogeneous systems [10] which we have adapted to non-isothermal calorimetric analysis of hydrogen sorption on these materials, assuming that the sorption process is a first-order reaction. Thus the relation $k = \Delta m W/(A - a)$ where k is the sorption rate constant, A the total area under the maximum in the thermogram, and a is the area under the maximum plotted during the duration of reaction, t (or to the temperature reached by time-programmed heating); $\Delta m W$ is the ordinate on the thermogram for any time t of the duration of the process, expressed in milliwatts (J/s, J/t). The plot of log k against $1/T$ is a straight line for first-order reactions and the slope $\Delta \log k/\Delta(1/T) = -E/R$ gives the activation energy E and the frequency factor of the process, Z.

3.1. Pd/WO_3–H_2 system

Fig. 1 shows thermograms (DSC) of the behaviour of WO_3 and Pd/WO_3 samples in a hydrogen flow. It is observed from thermogram 1 that WO_3 does not adsorb hydrogen and that Pd/WO_3 behaves as a very active adsorber of hydrogen, thermograms 2 to 4. The first heating of the Pd/WO_3 sample, represented by thermogram 2, shows that after an adsorption exo-maximum, a smaller endo-maximum occurs at about 420° C (693 K) corresponding to an irreversible process associated with a change in the structure of the newly formed hydrogen bronze, Pd/H_xWO_3. This endo-maximum only occurs during the first heating. Desorption of hydrogen occurs on exposure of the sample to nitrogen, air or argon atmospheres within a few minutes at an ordinary temperature, after cooling the sample in hydrogen. Further heating of the sample in a hydrogen flow repeats the adsorption with the same kinetic parameters, but without the endo-maximum, although the positions of the maxima on the thermogram are somewhat changed (thermograms 3 and 4). For the analysis of hydrogen adsorption process, non-isothermal DSC calorimetry was used. Analysis of thermograms 3 and 4 in Fig. 1 gives straight lines for the plot of log k against $1/T$, Fig. 2. An activation energy of $E = 54.706\,\mathrm{kJ\,mol^{-1}}$ was derived from the slope of $\Delta \log k/\Delta(1/T) = -E/R$, together with a frequency factor of $Z = 1.47 \times 10^4\,\mathrm{sec^{-1}}$, from thermogram 3 and $E = 52.456\,\mathrm{kJ\,mol^{-1}}$ and $Z = 4.85 \times 10^3\,\mathrm{sec^{-1}}$ from thermogram 4. On the basis of the linear dependence throughout the temperature range, Fig. 2, it can be stated that the reaction of hydrogen adsorption is a first-order one-step reaction. Enthalpies of adsorption were determined by

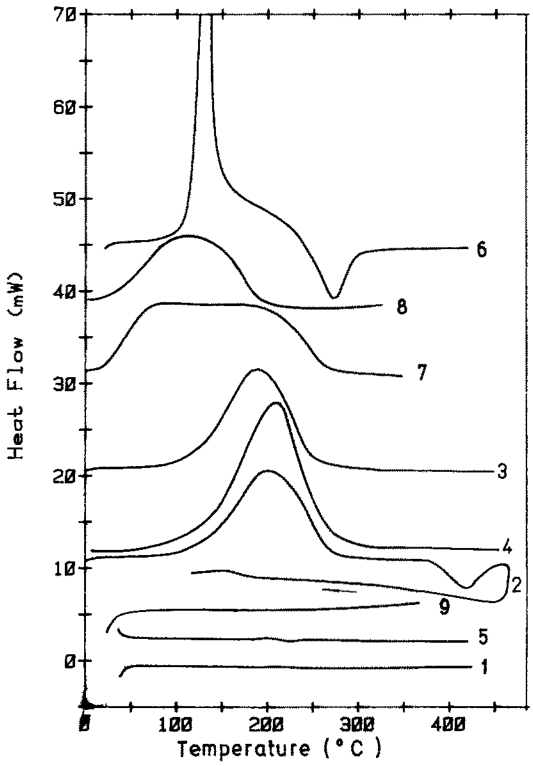

Figure 1 DSC thermograms. (1) WO_3 heated in H_2, $20\,\mathrm{K\,min^{-1}}$. Heating of Pd/WO_3 in H_2: (2) first heating $20\,\mathrm{K\,min^{-1}}$, (3) second heating $15\,\mathrm{K\,min^{-1}}$, (4) third heating $15\,\mathrm{K\,min^{-1}}$. (5) Heating of MoO_3 in H_2 $20\,\mathrm{K\,min^{-1}}$. Heating of Pd/MoO_3 in H_2: (6) first heating $20\,\mathrm{K\,min^{-1}}$, (7) second heating $20\,\mathrm{K\,min^{-1}}$, (8) second heating $5\,\mathrm{K\,min^{-1}}$; (9) heating in argon $20\,\mathrm{K\,min^{-1}}$.

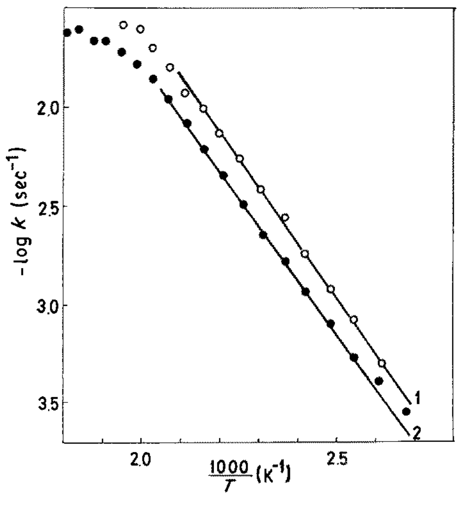

Figure 2 Activation energy plot of log k against $1/T$ corresponding (1) to thermogram 3 and (2) to thermogram 4 of Fig. 1.

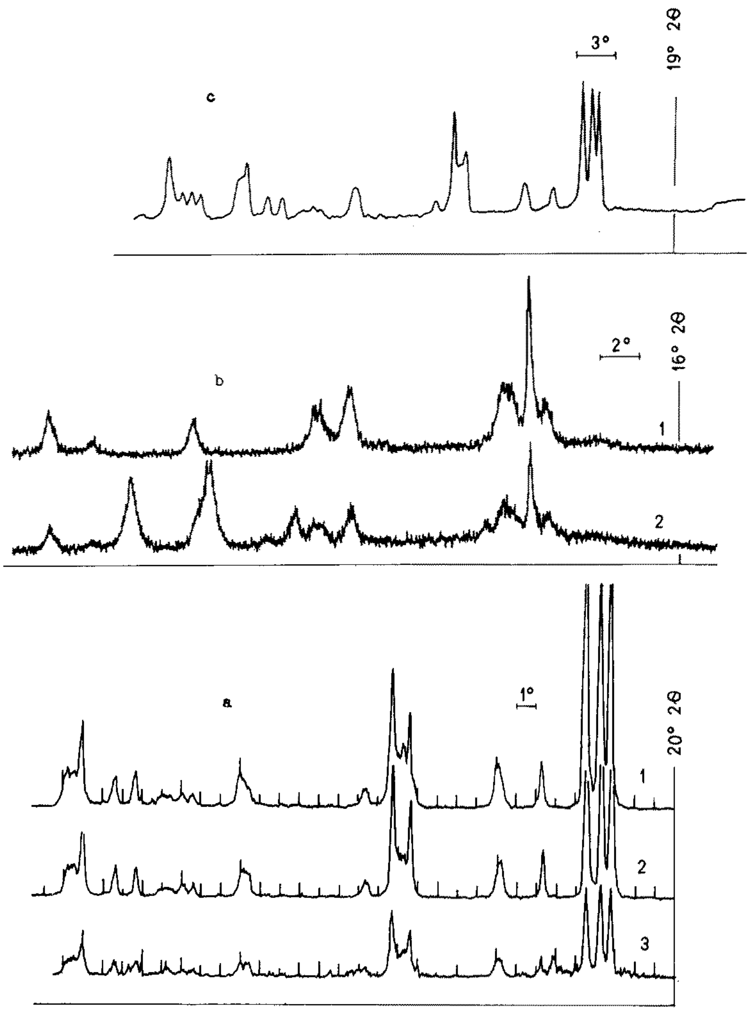

Figure 3 X-ray diffractograms. (a) (1) WO_3 heated in H_2 up to 723 K, (2) first heating of Pd/WO_3 in H_2 up to 733 K (thermogram 2, Fig. 1), (3) second heating of Pd/WO_3 in H_2 up to 673 K (thermogram 3, Fig. 1); (b) (1) Pd/WO_3 heated in H_2 up to 823 K and maintained at that temperature for 10 min, (2) the same sample at 823 K for another 20 min; (c) dark blue hydrogen bronze Pd/H_xWO_3 heated in oxygen at about 800 K for 15 min.

direct computer integration of the maxima on the thermograms. Maximum values derived were $-\Delta H = 200\,J\,g^{-1}$.

Bearing in mind that adsorption does not occur on pure WO_3, but only on samples containing palladium, it can be assumed that the adsorption process takes effect through the "hydrogen spillover" mechanism, meaning that atomic hydrogen is produced on dispersed palladium, which spills over to WO_3 forming, by adsorption, the hydrogen bronze, as the published data [6–9, 11] show for this and similar cases. Thus, the calculated magnitudes of activation energies and frequency factors refer to the process of the reaction of atomic hydrogen with WO_3.

X-ray analysis of the process of hydrogen adsorption on Pd/WO_3 samples shows that the change in colour of the newly formed hydrogen bronze from pale yellow to dark blue is followed by a change in structure, as presented in Fig. 3. As WO_3 does not adsorb (molecular) hydrogen, it is not subject to any structural changes, Fig. 3a, diffractogram 1. However, formation of Pd/H_xWO_3 bronze gradually changes the structure, diffractogram 2 and Fig. 3a. On longer heating of the incompletely formed Pd/H_xWO_3 (thermograms 2 and 3) at a constant temperature about 550° C (823 K) for 10 min, diffractogram 1, Fig. 3b, and a further 20 min, diffractogram 2, Fig. 3, a further change in structure is observed which would probably, by even longer heating, lead to the formation of the amorphous state. By heating of the hydrogen bronze formed in an oxygen atmosphere at about 550 to 600° C (823 to 873 K) hydrogen bronze is decomposed and the crystal powder of Pd/WO_3 is formed which is pale yellow in colour and has the monoclinic structure [12], as does the initial material, Fig. 3c.

3.2. Pd/MoO_3–H_2 system

Fig. 1 shows DSC thermograms of hydrogen sorption on the grey–white powder samples of Pd/MoO_3 and on MoO_3. It is observed that MoO_3 (thermogram 5) does not adsorb hydrogen while Pd/MoO_3 is involved in a complex sorption (reaction) process (thermograms 6 to 8). During the first heating in a hydrogen flow, thermogram 6 ($20\,K\,min^{-1}$) a sharp exo-maximum occurs in the initial part, which is further maintained in a rather wide form. The maximum ends at about 200° C (473 K) where the thermogram enters the endothermal area, forming an endo-maximum. No reversible process is observed on cooling in the same hydrogen atmosphere. In the process of hydrogen sorption, a product dark blue in colour, is formed which has a significantly enlarged volume with respect to the initial state. The product is very sensitive to the presence of oxygen at temperatures somewhat above ambient and is subject to violent ignition (oxidation) in air. When the sample cooled in hydrogen is exposed to air, nitrogen or argon for some time, hydrogen is desorbed from it, with no change of colour, and it is also able to readsorb hydrogen. During further heating of the same sample in the same way, a wide exo-maximum is derived, thermogram 7, without a sharp maximum in the initial part, as in thermogram 6. These sorption–desorption procedures repeated in the same way give the same wide maxima as those observed from thermogram 7. However, thermogram 8 which is derived by slower heating, 5 K min^{-1}, shows a narrower maximum due to slower heating which accounts for the two steps of the adsorption process becoming thermally closer to one another. It is also observed that the maxima in thermograms 7 and 8 begin at a lower temperature than that in thermogram 6, probably due to the process of "activation" and transition of the sample to the amorphous state during a process that corresponds to thermogram 6 (first heating).

In order to elucidate the nature of the process that takes place in the course of heating of the Pd/MoO_3 sample in hydrogen, following experiments were undertaken.

1. A certain amount of Pd/MoO_3 was heated in the DSC cell only up to 125° C (393 K), i.e. to the end of the first sharp endo-maximum.

2. The same sample was cooled in the DSC cell in hydrogen down to ambient temperature and heated again in an air flow. A very sharp exo-maximum was observed due to a very violent reaction which starts at about 20 to 30° C (293 to 303 K) when the flow of hydrogen is substituted by the flow of oxygen (O_2).

3. On thorough investigation, this process was attributed to the reaction of oxygen from air with the adsorbed hydrogen on the sample, apparently forming water.

4. The same sample, cooled in air in the DSC cell and then heated again in a hydrogen flow up to 125° C, adsorbs hydrogen vigorously, as during the first heating, but the process begins at a somewhat lower temperature (by this treatment the sample became more active) so that the sharp exo-maximum appears at about 50° C.

5. Heating of the initial (new) sample in argon or air flow up to 350° C produces no effect or change in colour, nor is any endo-maximum observable at about 255° C. Repeated heating of the same sample in a hydrogen flow yields a thermogram identical to thermogram 6 in Fig. 1, with an endothermal maximum.

6. As with the Pd/WO_3 system, the endo-maximum only appears during the first heating in hydrogen, when the sample changes colour and when initially a partial (reversible) reduction occurs, followed by hydrogenation, i. e. hydrogen adsorption through the "spillover" mechanism, which results in the formation of hydrogen bronze Pd/H_xMoO_3.

X-ray analysis, Fig. 4a, shows that the original non-hydrogenated Pd/MoO_3 has the same structure as MoO_3. Pd/MoO_3 heated in hydrogen up to 150° C shows the decomposition of the lattice due to the

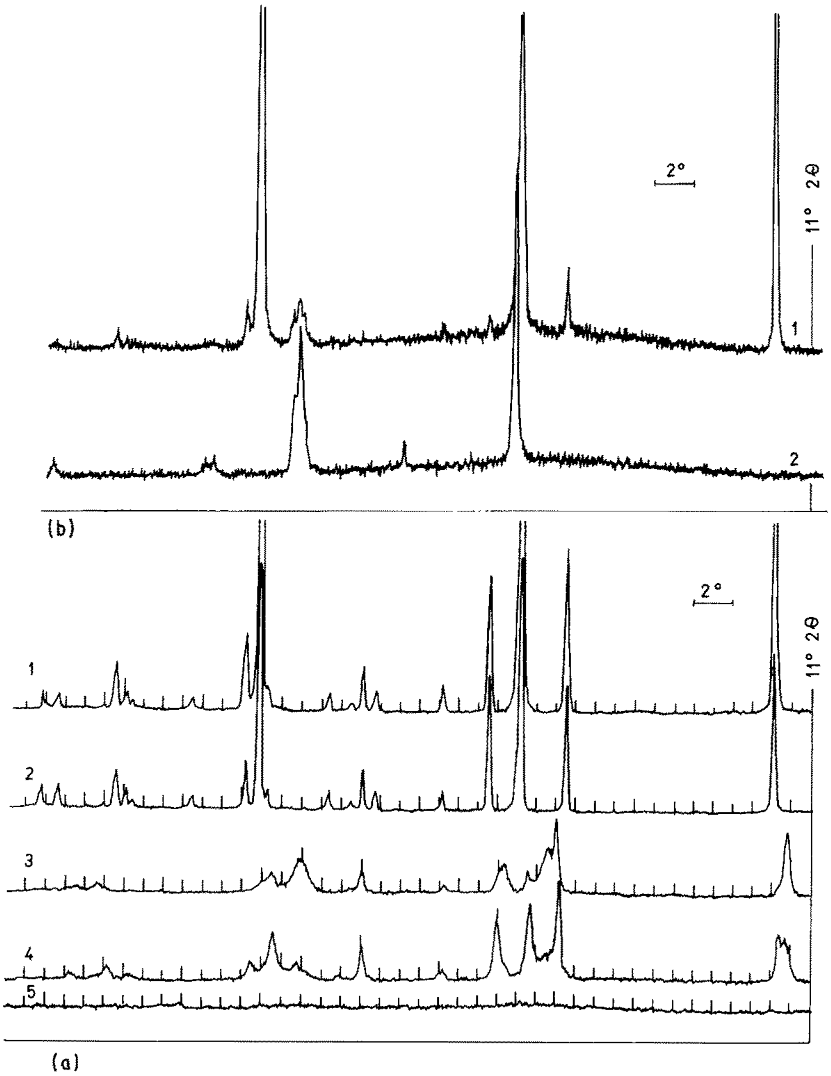

Figure 4 X-ray diffractograms (a) (1) MoO_3, (2) Pd/MoO_3, (3) Pd/MoO_3 heated in H_2 up to 423 K, (4) Pd/MoO_3 heated in H_2 up to 510 K, (5) Pd/MoO_3 heated in H_2 up to 623 K (thermogram 6, Fig. 1); (b) (1) crystalline Pd/MoO_3 after cycling (see text) ended by 10 min in H_2 at 723 K, (2) the same sample maintained in hydrogen at 723 K for another 20 min; (c) cycling Pd/MoO_3 in H_2 and O_2 in the TGA cell: (1) last heating in O_2 up to 820 K, (2) last heating of the same sample in H_2 up to 820 K; (d) amorphous Pd/H_xMoO_3 after heating in O_2 at 723 K (see TGA thermogram in Fig. 6b).

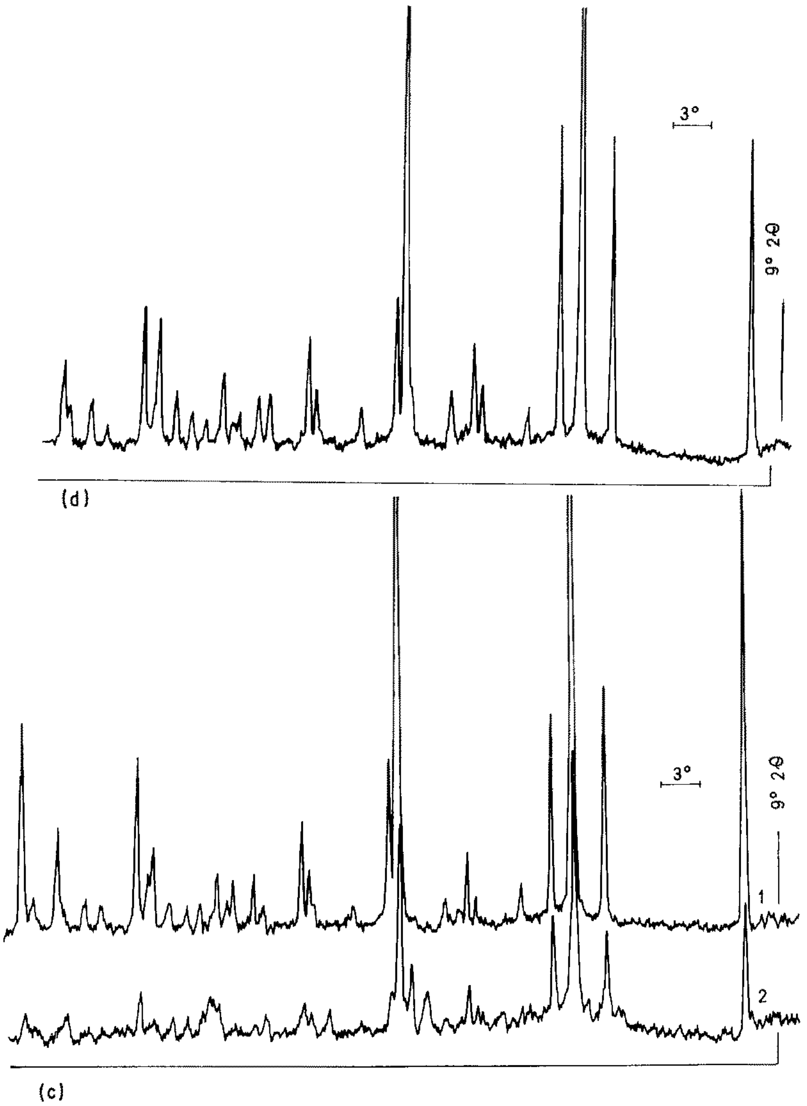

Figure 4 Continued.

process of hydrogen adsorption. Further heating to 237° C is apparently followed by further decomposition of the structure, and heating up to 340° C (above the temperature of the endo-maximum) leads to the total decomposition of the structure which is then completely substituted by the amorphous state. The endo-maximum represents an irreversible process associated with the structural change. Heating of this sample in air produces a violent oxidation (water formation is observable) and, after cooling in the DSC cell in an air flow, the sample is capable of adsorbing hydrogen, producing a thermogram identical to thermogram 6 in Fig. 1, but without the endo-maximum.

Hydrogen adsorption kinetics on the Pd/MoO_3 sample was analysed in the same manner as in the case of the Pd/WO_3 sample. The plot of log k against $1/T$ is given in Fig. 5 and corresponds to thermogram 8 of Fig. 1, i.e. to the second heating of the sample in hydrogen 5 K min^{-1} (after desorption of hydrogen

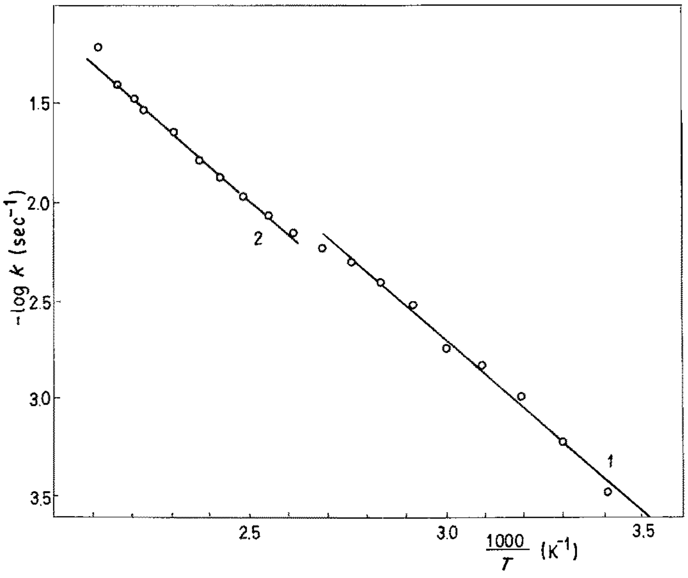

Figure 5 Activation energy plot of log k against $1/T$ corresponding to thermogram 8 of Fig. 1.

adsorbed in the first heating). A broken line is derived with two close slopes, which, in addition to the appearance of the thermograms 6 and 7, confirms that the process takes place in two steps and as a first-order reaction. From the slopes of the lines, -1.73×10^3 for the first and -1.73×10^3 for the second step, the activation energies are derived: $E_1 = 33.19\,\mathrm{kJ\,mol^{-1}}$ for the first and $E_2 = 33.51\,\mathrm{kJ\,mol^{-1}}$ for the second step, together with the correponding frequency factors $Z_1 = 3.26 \times 10^2\,\mathrm{sec^{-1}}$ and $Z_2 = 2.42 \times 10^2\,\mathrm{sec^{-1}}$.

It seems that the heat (enthalpy) of hydrogen adsorption, after the first heating when the reduction takes place (reaction with oxygen), still depends on the oxygen present (adsorbed during the process of hydrogen desorption when the DSC cell is opened and the sample exposed to air). The highest value derived for the enthalpy of hydrogen adsorption in the third adsorption process was $1298\,\mathrm{J\,g^{-1}}$, when a wide maximum was derived in the thermogram, without any sharp maximum.

In order to elucidate further the process of sorption–desorption of hydrogen on Pd/MoO_3 in a hydrogen atmosphere and the process of oxidation (adsorption) of oxygen on the same hydrated and partly reduced sample of Pd/MoO_3, thermogravimetric (TGA) studies were carried out.

Thermogravimetric observation of the process by alternately heating the same Pd/MoO_3 sample in hydrogen and (after cooling in hydrogen and flushing the unit with pure argon) oxygen, shows the following results.

1. During the first heating in a hydrogen flow, at 80° C Fig. 6a, an exothermal process of hydrogen oxidation by oxygen has already taken place with local overheating of the sample. The water which is formed leaves the sample, but is probably condensed on the walls of the platinum vessel, thus obstructing the registration of its quantity on the TG thermogram. This process corresponds to the first and sharp exo-maximum on the DSC thermogram, ending at 120° C (393 K).

2. On further heating of the same but thermally stabilized sample, a small increase in weight is produced over an interval 10 to 20° C wide after which the weight remains unchanged up to about 230° C (503 K), when a steep fall to about 300° C (573 K) is observed. Further heating produces a slow fall. The small increase in weight (after reduction with hydrogen) is attributed to adsorption of hydrogen and formation of hydrogen bronze (a small change in weight due to the small weight of hydrogen). The area of the increase in weight does not correspond completely to the exo-maximum on the DSC thermogram, which can be explained by the fact that the process of hydrogen adsorption is still accompanied by the reduction and formation of water which leaves the sample and can be observed visually in the condensed form in the TG cell. The fast, followed by a slow, fall of weight with further heating is attributed to the further formation of hydrogen bronze and the process of (oxide) reduction which forms water that evaporates and condenses on the cooler walls of the TG cell.

3. After heating in hydrogen, points 1 and 2, the unit is flushed with pure argon (to avoid the catalytic reaction of the introduced oxygen with the residual hydrogen) followed by a heating of the same sample in an oxygen flow, Fig. 6b. A very exothermal process occurs at once, with local overheating of the sample, at a temperature below 100° C (373 K), together with a weak increase in weight and an apparent formation of water. A decrease in weight follows, in two temperature ranges up to 320° C (593 K), which continues to a fast increase in weight that ends at about 400° C (673 K) with the final weight of the sample being higher than its initial weight. We believe that the first small increase in weight is the result of the formation of water which, at this temperature, does not evaporate quickly. The following decrease in weight can be attributed to the reaction of oxygen with hydrogen bronze and adsorbed hydrogen, resulting in the formation of water which evaporates from the sample and condenses on cooler parts of the TG cell. The increase in weight after the full consumption of hydrogen corresponds to a stepwise oxidation of the sample up to the highest oxidation state. After cyclic heating in hydrogen and oxygen in turn (ending with heating in oxygen) the sample attains the original grey-white colour and gives DSC thermograms in hydrogen of the same appearance as thermogram 6 in Fig. 1, but without the endo-maximum. By this cycling the original sample is transformed to the amorphous state at the end of the first heating in hydrogen and then attains the crystal structure and the original grey–yellow colour after heating in oxygen, as observed from the diffractograms in Fig. 4d.

X-ray investigations of the samples subjected to cycling with H_2–O_2 in the TG cell indicate that the crystal structure of the samples whose cycle ended in hydrogen have a somewhat changed (weaker) reflectivity than the samples whose cycle ended in oxygen. It seems that the crystal sample formed by the cycling process and exposed to hydrogen for a longer time, at a raised temperature, as happens in the cycling process, changes its structure, as is observed in Fig. 4b.

A further question raised was whether the amorphous molybdenum hydrogen bronze showed signs of crystallization on longer exposure to a hydrogen atmosphere. To answer this, the amorphous Pd/MoO_3 sample formed was initially heated in hydrogen for 50 min at 475° C (748 K) in the first instance, Fig. 7, diffractogram 1, and then for 2 h at 500° C (773 K), diffractogram 2 in Fig. 7. A clear difference is apparent in the growth of the crystal component which gives reflections at 43° $2\theta^1$, showing that the amorphous hydrogen bronze can attain the crystal state if heated in hydrogen long enough.

Qualitatively similar results were also obtained by electron microscopy. According to these, Pd/MoO_3 heated in hydrogen forms amorphous hydrogen bronze which shows signs of crystallization on further exposure to hydrogen, while heating in air results in complete crystallization and decomposition of the bronze, as quantitatively proved by TGA and X-ray analysis.

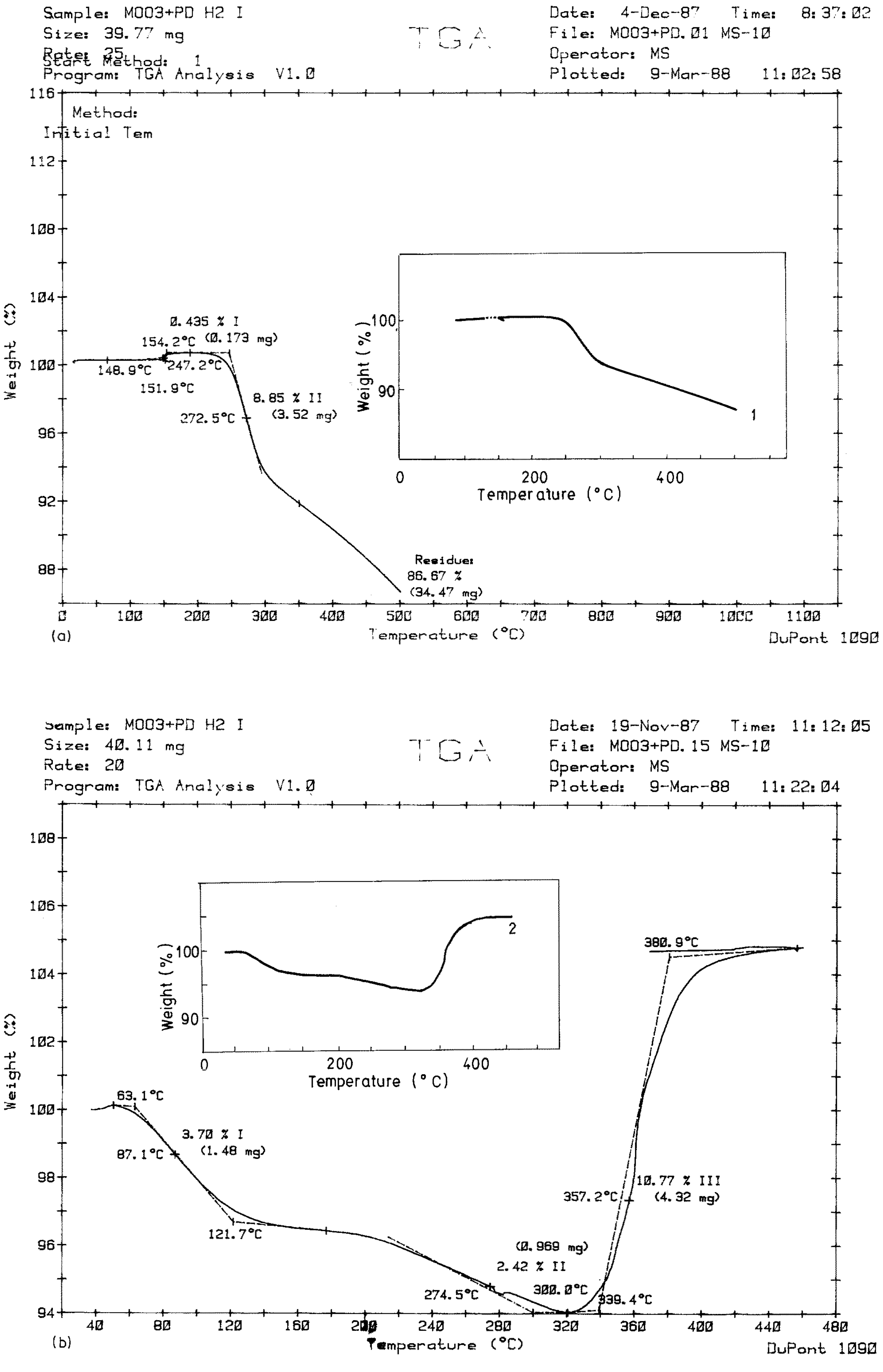

Figure 6 TGA thermograms: (a) Pd/MoO$_3$ in H$_2$, (b) the same sample in O$_2$, 20 K min^{-1}. (The original and enlarged thermograms with analytic processing are presented.)

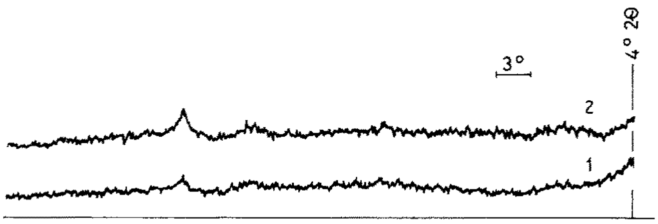

Figure 7 X-ray diffractograms of amorphous Pd/H_2MoO_3: (1) heated in H_2 at 475° C for 50 min; (2) heated in H_2 at 500° C for 2 h.

4. Conclusions

1. Hydrogen sorption on Pd/WO_3 and Pd/MoO_3 with 0.1% Pd takes place through the "hydrogen spillover" mechanism in the range of temperatures from ambient to 620 K on Pd/WO_3 and to 680 K on Pd/MoO_3, producing corresponding hydrogen bronzes of dark blue colour. Desorption of hydrogen takes place, with no change in colour, by exposing the sample to air, oxygen, nitrogen or argon at ambient temperature. Atomic hydrogen, derived in the spillover process, is adsorbed by the Pd/WO_3 bronze in one step in a first-order reaction for which the kinetic and thermal parameters were determined. Sorption of atomic hydrogen by the Pd/MoO_3 bronze takes place in two steps. In the first step, beside sorption, a reduction of the oxygen present takes place producing water, which corresponds to a very sharp exo-maximum. Kinetic and thermal parameters were also derived for both steps. Hydrogen sorption by Pd/WO_3 changes its structure. Hydrogen sorption by Pd/MoO_3 breaks the crystalline structure of WO_3 and produces amorphous hydrogen bronze of voluminous form.

2. Cyclic heating of Pd/MoO_3 sample in the TGA cell in hydrogen and oxygen flows in turn, with previous cooling to ambient temperature in the corresponding gas and flushing with argon prior to changing the gases, it was shown that the hydrogen bronze formed reacts very vigorously with the introduced oxygen, producing water. In the same way, after heating in oxygen the product formed reacts vigorously with hydrogen, also producing water and hydrogen bronze. Amorphous hydrogen bronze Pd/H_xMoO_3 heated in oxygen to 720 K changes its dark-blue colour to (original) grey reattaining the crystalline state, at which point the sample is maximally oxidized. Further heating in hydrogen produces the amorphous state of the hydrogen bronze.

On heating in oxygen to 800 K, hydrogen bronze, Pd/H_xWO_3 is decomposed and transformed into the Pd/WO_3 bronze which is yellow in colour and monoclinic in structure.

On longer exposure to hydrogen at temperatures above 500° C (773 K) amorphous hydrogen bronze shows a tendency to crystallize.

At the present time we are trying to solve the structure change influenced by the sorption–desorption processes at different temperatures.

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Received 24 June
and accepted 8 December 1988