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THE INFLUENCE OF SURFACE REACTIONS ON ANALYTICAL THERMOGRAVIMETRIC RESULTS

M VALIGI and D GAZZOLI

Centro di Studio su "Struttura ed Attività Catalitica di Sistemi di Ossidi" C.N.R., Istituto di Chimica Generale ed Inorganica, Università di Roma, Rome (Italy)

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ABSTRACT

Two examples are given to show the influence of surface reactions on analytical thermogravimetric results The first concerns the effect of the crucible material on the reduction of rhenium heptoxide by hydrogen In the second, the effect of a strong metal-support interaction on the evaluation of the average oxidation number of rhodium present in small percentage in the system RhO_x–TiO_2 is discussed

INTRODUCTION

In the course of investigations of the surface chemistry of rhenium oxide [1,2], and of solid solution formation in the system titanium dioxide–rhodium oxide [3], it was found that the thermogravimetric behaviour pointed to the occurrence of surface processes not accounted for by simple stoichiometry. In view of the extensive use of thermogravimetry in analytical problems, and of the precision now obtainable with this technique, we thought it of interest to discuss these two examples which draw attention to the need to understand the surface reaction before the analytical method is accepted. In the first example, the influence of the crucible material on the reduction of rhenium heptoxide by hydrogen is shown; in the second, the determination of the average oxidation state of rhodium present in small percentage in the system RhO_x–TiO_2 is illustrated. The case of tin in the system SnO_x–TiO_2 (no surface reaction occurring) is also briefly discussed.

EXPERIMENTAL

Only a brief illustration of the materials and of the method are given, since they are fully described elsewhere.

Materials

Re_2O_7 (Merk) was used. The as-received oxide was anhydrous, but on standing in the atmosphere it takes up water, being hygroscopic [4].

Titanium dioxide containing tin or rhodium was prepared by an impregnation technique followed by a thermal treatment in air at 1000°C for 5 h [3,5].

Apparatus

The thermogravimetric measurements were performed with a Cahn RG electrobalance, adjusted to a maximum weight change of 100 mg and a sensitivity of 0.01 mg. The crucible was either of platinum or silica. A silica reactor tube, 26 mm in outer diameter and 500 mm in length was connected in the upper part to the vessel containing the balance and in the lower part, via a valve, to a flowmeter. The balance vessel was connected to a vacuum line and a gas supply system. This allowed the entire system to be evacuated and filled with the desired atmosphere. A flow of hydrogen or oxygen (from cylinders, dried through a two-trap system cooled by liquid nitrogen for hydrogen and liquid oxygen for oxygen) was then established (24 ml min^{-1}) and the temperature raised. The sample temperature was measured with a thermocouple placed inside the reactor tube close to the crucible. The furnace temperature was automatically controlled so that the sample temperature rose linearly up to 900°C at a heating rate of 3°C min^{-1}.

RESULTS AND DISCUSSION

Reduction of Re_2O_7

To remove water before the thermogravimetric experiment in hydrogen, the sample was dried at 110°C with dry oxygen inside the apparatus for 1 h. After cooling at room temperature, the oxygen was removed by evacuation and then hydrogen was admitted. Figure 1 shows the thermogravimetric curves for Re_2O_7 performed in a hydrogen stream by using a silica (full dots) or a platinum (open dots) crucible.

The results obtained by using the two types of crucibles are markedly different. With the platinum container a weight loss starting at 120°C and ending at 250°C is observed. The per cent weight loss, $\Delta\%$, amounts to 23.30% indicating that the process taking place is the reduction of Re_2O_7 to metallic rhenium (calculated weight change per cent = 23.18%). By using the silica crucible the weight decrease starts at a somewhat higher temperature and a higher weight loss is obtained ($\Delta\% = 40$). In addition, as already noticed by Ratner et al. [6], a thin film having a metallic lustre was observed on the reactor wall. This anomalous, higher weight loss observed with the silica crucible, has been ascribed to partial volatilization of Re_2O_7 [1]. Because of its crystal structure [7], this oxide is, indeed, highly volatile [8] and during the

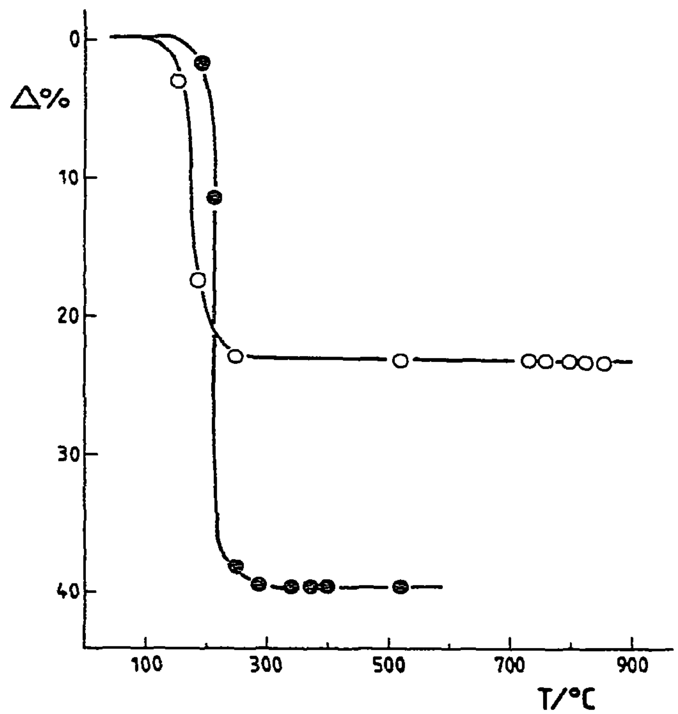

Fig 1 Thermogravimetric weight loss per cent, Δ%, vs T/°C for Re_2O_7 heated in hydrogen atmosphere ○, platinum crucible, ●, silica crucible

thermogravimetric experiment in hydrogen it is partially lost before the reduction takes place. The volatilized oxide is then reduced in the vapor phase to the lower oxide and to metal causing the metallic, lustre on the cold walls. To avoid loss *via* volatilization, it is necessary to increase the rate of reduction with respect to that of volatilization. This is precisely what happens when the platinum crucible is used. In this case, in fact, a spill-over effect is present [1]. The hydrogen atomically adsorbed on platinum increases the reduction rate and Re_2O_7 is no longer lost. The spill-over effect on the reduction of Re_2O_7 in the presence of platinum has been reported [9]. The interference of surface spill-over phenomena is therefore strongly influencing the results of the thermogravimetric analysis.

Determination of the average oxidation state of the impurity in the SnO_x–TiO_2 and RhO_x–TiO_2 systems

The characterization of the SnO_x–TiO_2 and RhO_x–TiO_2 samples by X-ray diffraction techniques, chemical analysis, thermogravimetric measurements and ESR spectroscopy has been reported previously [3,5]. In the case of SnO_x–TiO_2 [5], Sn (IV) is incorporated in solid solution in TiO_2 (rutile). When heated in a hydrogen atmosphere in a thermogravimetric apparatus, a loss in weight is observed in the range 600–750°C caused by the reduction of Sn(IV) to metallic tin. In the system RhO_x–TiO_2 [3], rhodium is present in the 3+ oxidation state both as a separate

TABLE 1

Analytical and thermogravimetric data for the system SnO_x–TiO_2

Sample no	Sn (%)	Δ (%)
1	1.68±0.10	0.45±0.02
2	2.96±0.10	0.78±0.02
3	3.87±0.15	1.05±0.02
4	5.26±0.20	1.40±0.02

phase, Rh_2O_3, and in solid solution. In addition, a small amount of rhodium is present as Rh(II) in solid solution. Thermogravimetric curves, performed in hydrogen, show that the different rhodium species are reduced to the metallic state in the temperature range 150–720°C Since below 750°C no decrease in weight is detected when undoped TiO_2 is heated in a hydrogen atmosphere, both for the system containing tin and for that containing rhodium it is possible to evaluate the average oxidation number of the added impurity, $\bar{n}$, by combining thermogravimetric and chemical analysis results (Tables 1 and 2). The relation to be applied is

$$\bar{n} = \frac{\Delta\%}{\%\mathrm{M}} \times \frac{\mathrm{M\ atomic\ weight}}{\mathrm{O\ atomic\ weight}/2} \qquad (1)$$

where M = tin or rhodium, respectively.

The results obtained are plotted in Fig. 2. Curve a shows that tin is indeed present as Sn(IV) confirming previous data [5,10,11].

By contrast, when applying the same procedure to the rhodium doped TiO_2 system an erroneous conclusion is reached. In fact, by inserting in eqn. (1) the values of Δ% and %Rh, listed in Table 2, the values of $\bar{n}$ shown in Fig. 2 (curve b) are obtained. The curves seem to indicate that for dilute samples Rh(IV) is present. However, as discussed in a previous paper [3], only Rh(III) and a small fraction of Rh(II) are found in the samples. The discrepancy may be accounted for on the basis of a phenomenon found first by Tauster [12]: when rhodium species are reduced in contact with titanium dioxide a strong metal-support interaction develops. This interaction is confirmed in several other papers [13–16]. It involves a reduction of

TABLE 2

Analytical and thermogravimetric data for the system RhO_x–TiO_2

Sample no	Rh (%)	Δ (%)
1	0.85±0.03	0.27±0.02
2	1.76±0.04	0.53±0.02
3	3.59±0.13	0.92±0.02
4	5.34±0.20	1.48±0.02
5	10.65±0.35	2.63±0.02
6	11.85±0.40	2.90±0.02

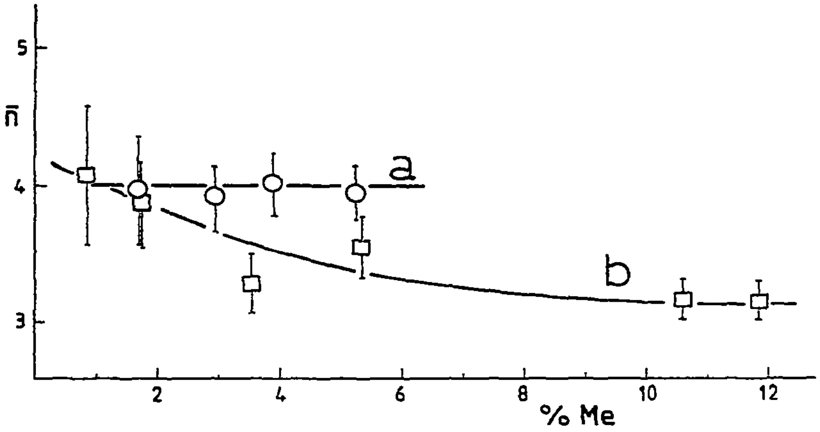

Fig 2 The average oxidation number, n̄, of the added impurity, M, in the MO_x–TiO_2 system vs the M content The M concentration is expressed as per cent by weight ○, M=Sn. □, M=Rh

TiO_2 as directly shown by electron microscopy in the case of platinum supported on TiO_2 [7,8]. Therefore a higher loss in weight is measured with respect to the value expected from the reduction of the rhodium species. The effect is more evident at lower concentrations because it is a surface effect, and therefore depends on the possibility of contact between rhodium and TiO_2 surface. Its extent is correlated with the specific surface area. Since these samples have very low surface area (1 m^2 g^{-1}), the maximum amount of rhodium in contact with the support is around 1% by weight [3]. Therefore, for samples with rhodium content exceeding this value, the value of $\bar{n}$ is found to decrease (approaching the value of 3) as the rhodium content increases. Here again we have a surface phenomenon which can interfere with the determination of the amount of supported, or dissolved, metal oxides.

As a concluding remark, the two examples given point to the need to carefully monitor the presence of surface reactions interfering with the thermogravimetric determination.

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