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A structural, thermogravimetric and ESR study of the RhO_X-TiO_2 system

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Titanium dioxide samples containing a few per cent of rhodium oxide, heated in air at 1273 K, have been investigated in order to study the formation of solid solutions. The results, monitored by X-ray diffraction, thermogravimetry in a hydrogen stream and ESR spectroscopy, show that rhodium is present both as separate phase (Rh_2O_3) and in solid solution in the rutile structure. The incorporated rhodium is mainly present in the 3 + oxidation state, only a small fraction being present as Rh(II). Rh_2O_3 and the rhodium species in solid solution are reduced by hydrogen to metal in different temperature ranges. By combining thermogravimetric and analytical data, the average oxidation state of rhodium, $\bar{n}$, has been evaluated. The variation of $\bar{n}$ with the rhodium content has been accounted for on the basis of a strong metal–support interaction developing with the reduction. This interaction affects the metal dispersion.

1. Introduction

Systems based on rhodium supported on titanium oxide are receiving increasing attention as potential heterogeneous catalysts [1–4]. Interaction between the support and the rhodium oxide would be better understood if the tendency to form solid solutions could be proved. RhO_2 is reported to have a rutile-type structure [5], to be stable in air up to 953 K [5] and the Rh(IV) ionic radius ($r_{Rh(IV)} = 0.060$ nm [6]) is very close to that of Ti(IV) ($r_{Ti(IV)} = 0.0605$ nm [6]). However, information on solid-solution formation between rhodium oxide and titanium dioxide is lacking. It should be noted that the study of solid solutions can also provide useful information on surface chemistry problems, e.g., as regards the dispersion of metals, and photo- and electro-catalysis problems. The present study was undertaken in order to check the possibility of incorporation of rhodium ions into the TiO_2 (rutile) structure and, in the affirmative case, to determine the oxidation state of the dissolved species. The study has been performed by using several techniques: X-ray diffraction, thermogravimetry in a hydrogen atmosphere, chemical analysis and ESR spectroscopy.

2. Experimental procedure

2.1. Sample preparation

Titanium dioxide, prepared by hydrolysis and oxidation of $TiCl_3$ (supplied by Erba RP) as previously described [7], was impregnated with an appropriate volume of rhodium nitrate solution. The latter was obtained by dissolving $Rh(NO_3)_3 \cdot 6H_2O$ (supplied by Fluka) in water. The slurry was mixed and dried at 383 K. The powder was then ground in an agate mortar, heated in air at 773 K for 2 h, re-ground and finally heated at 1273 K for 5 h in air. At the end of the thermal treatments the samples were cooled slowly to room temperature in the furnace. Two different series of samples were prepared. The first series, Series A, was obtained by using a non-standardized rhodium solution; in this case the content of the rhodium in the samples was determined by chemical analysis as described below. The second series of samples, Series B, was prepared by dissolving a weighed amount of $Rh(NO_3)_3 \cdot 6H_2O$ in water and adding a known amount of starting titanium oxide. The rhodium content in the starting salt was determined thermogravimetrically by measuring the weight-loss accompanying the heating of the salt to 1173 K in a stream of hydrogen in the thermogravimetric apparatus.

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TABLE I Thermogravimetric and analytical data for the rhodium-doped titanium dioxide samples

Samples	Weight-loss when sample heated in H_2 (%)		Rhodium content			
	423–993 K	423–623 K	$[Rh]_{tot}$†	$[Rh]_{tot}$(wt%)	$[Rh]_{Rh_2O_3}$(wt%)	$[Rh]_{ss}$†
TRh 0.7 A	0.27	0.02	0.67	0.85	0.08	0.60
TRh 1.5 A	0.53	0.04	1.40	1.76	0.17	1.25
TRh 3 A	0.93	0.04	2.92	3.59	0.17	2.77
TRh 3 A‡	0.87	0.07	2.89	3.55	0.30	2.63
TRh 4.5 A	1.48	0.06	4.44	5.34	0.26	4.21
TRh 4.5 A‡	1.44	0.04	4.27	5.14	0.17	4.12
TRh 9.5 A	2.63	0.37	9.53	10.65	1.59	7.93
TRh 11 A	2.90	0.20	10.79	11.85	0.86	9.88
TRh 0.7 A*	0.28	–	0.67	0.85	–	0.67
TRh 9.5 A*	2.48	0.40	9.53	10.56	1.71	7.81
TRh 11 A*	2.60	0.47	10.79	11.85	2.01	8.71
TRh 1 B	0.39	0.02	1.04	1.31	0.08	0.97
TRh 3 B	0.95	0.05	2.71	3.34	0.21	2.53
TRh 8 B	2.21	0.30	6.95	8.05	1.28	5.80
TRh 1 B*	0.34	–	1.04	1.31	–	1.04
TRh 3 B*	0.91	0.04	2.71	3.34	0.17	2.56
TRh 8 B*	1.90	–	6.95	8.05	–	6.95

†Rhodium atoms per 100 titanium ions.
‡Different preparation.

Several samples were subjected to a second heating in air at 1273 K for 48 h. At the end of this thermal treatment the samples were rapidly cooled to room temperature.

The specimens were designated as TRh; the figure after the symbol indicates the nominal rhodium content expressed as Rh atoms per 100 Ti atoms. The letter A or B specifies the two series of samples. The samples re-heated at 1273 K for 48 h are indicated by an asterisk.

Undoped TiO_2 was prepared following the same procedure, the impregnation being performed with water.

The samples containing rhodium appeared brown, the colour intensity increasing with the concentration; undoped TiO_2 was white.

2.2. Determination of rhodium

For the samples of Series A the total rhodium content was determined spectrophotometrically by the $SnCl_2$ method [8]. Weighed portions of the sample were fused with $KHSO_4$ in a silica crucible. After cooling the solid was dissolved in water and the solution analysed spectrophotometrically at $\lambda = 470\,\mu m$. The standard solution, prepared using a standard 1000 ppm rhodium nitrate solution (supplied by Fisher) contained TiO_2 (fused with $KHSO_4$) in a concentration comparable to that present in the solution of the samples. Each specimen was analysed twice; the results agreed within 4%.

For the samples of Series B the final rhodium content was obtained from the nominal rhodium and TiO_2 contents, the latter being corrected for the decrease in weight resulting from the thermal treatment at 1273 K. The rhodium concentrations for the different samples of both Series A and B are reported in Table I.

2.3. Thermogravimetric analysis

Thermogravimetric determinations were carried out on a Cahn RG electrobalance. During the experiment the sample was kept in a constant flow of hydrogen (24 ml min^{-1}). The temperature was raised to 1273 K using a linear programmer at a rate of 3° min^{-1}. The weight was measured to an accuracy of 0.02 mg.

2.4. X-ray measurements

The rutile unit-cell parameters were measured following the procedure previously described [7], by using a Debye–Scherrer camera, having an internal diameter of 114.6 mm, and $CoK\alpha_1$ (Fe-filtered) radiation. The position of the reflections on the X-ray spectra was read to an accuracy of 0.05 mm. The estimated error in the cell parameter, a, and in the axial ratio, $C = c/a$, were $\pm 1.10^{-5}$ nm and $\pm 1.10^{-4}$, respectively.

TABLE II TiO_2 unit cell parameter, *a*, axial ratio, *C*, and phase analysis for the TRh samples.

Samples	a_{294} (nm)	*C*	Phases
TiO_2	0.459 28	0.6443	R†
TRh 0.7 A	0.459 42	0.6441	R
TRh 1.5 A	0.459 64	0.6438	R
TRh 3 A	0.459 92	0.6434	R, Rh_2O_3 (traces)
TRh 4.5 A	0.460 13	0.6433	R, Rh_2O_3
TRh 9.5 A	0.460 32	0.6432	R, Rh_2O_3
TRh 11 A	0.460 56	0.6430	R, Rh_2O_3
TRh 0.7 A*	0.459 46	0.6442	R
TRh 9.5 A*	0.450 70	0.6423	R, Rh_2O_3
TRh 11 A*	0.460 82	0.6420	R, Rh_2O_3
TRh 1 B	0.459 48	0.6443	R
TRh 3 B	0.460 03	0.6436	R, Rh_2O_3
TRh 8 B	0.460 30	0.6431	R, Rh_2O_3
TRh 1 B*	0.459 59	0.6441	R
TRh 3 B*	0.459 93	0.6433	R, Rh_2O_3 (traces)
TRh 8 B*	0.460 62	0.6424	R

†R = rutile.

The same camera was used for the phase analysis. In this case CuKα (Ni-filtered) radiation was used.

2.5. ESR spectra

The ESR measurements were performed on Varian X-band spectrometers mainly at 77 K, and occasionally at room temperature (using a Varian E-9) and at 4.2 K (using an E-12). The absolute number of spins was determined at 77 K from electronically integrated spectra, using Varian "Strong pitch" (3×10^{15} spin cm^{-1}) as a standard.

3. Results

3.1. X-ray analysis

The results of the rutile unit cell parameters, a, and axial ratio, *C*, are listed in Table II. The results of the phase analysis are also shown in Table II. It may be seen that the addition of rhodium affects both *a* and *C*. For the more diluted specimens, only rutile reflections are present in the powder diffraction spectra. For samples with a higher rhodium content the lines of Rh_2O_3 are also detected. In this case a difference in the Rh_2O_3 crystalline modification is observed according to the procedure of the thermal treatment. Samples heated at 1273 K for 5 h contain hexagonal Rh_2O_3 [9–10], whereas those heated for 48 h (asterisks) contain both hexagonal and orthorhombic [11] Rh_2O_3. In Table III the X-ray spectra of TRh 11 A and TRh 11 A* are shown as typical examples. The transformation of hexagonal to orthorhombic Rh_2O_3 is quite slow at 1273 K. In fact the presence of the orthorhombic phase depends only on the time of treatment at 1273 K and not on the cooling procedure (slow or rapid cooling). This point was tested by heating pure hexagonal Rh_2O_3 (obtained by decomposition of rhodium nitrate at 973 K) in air at 1273 K for 3 h and 48 h. The X-ray spectra of the sample

TABLE III X-ray diffraction spectra of the samples TRh 11 A and TRh 11 A*

TRh 1 A		TRh 11 A*		TiO_2 (rutile)†		Rh_2O_3 (hexagonal) [10]		Rh_2O_3 (orthorhombic [11]	
Intensity‡	*d* value (nm)	Intensity	*d* value (nm)	Intensity	*d* value (nm)	Intensity	*d* value (nm)	Intensity	*d* value (nm)
vw	0.364	vw	0.365		–	53	0.368	15	0.368
	–		–		–		–	11	0.3623
vs	0.324	vs	0.324	100	0.324		–		–
w	0.272	w	0.275		–	88	0.2738	31	0.2722
	–		–		–		–	4	0.2673
	–	w	0.262		–		–	100	0.2619
w	0.254	vw	0.257		–	100	0.2567	39	0.2574
ms	0.248	ms	0.249	41	0.2489		–		–
	–		–		–		–	2	0.2376
mw	0.229	w	0.230	7	0.2297		–		–
	–		–		–	7	0.2242		–
m	0.218	m	0.219	22	0.2188		–	6	0.2188
	–		–		–	6	0.2116	4	0.2104
mw	0.205	mw	0.205	9	0.2054		–		–
w	0.186	vw	0.187		–	37	0.1869	27	0.1869
	–		–		–		–	10	0.1836
vw	0.171		–		–	53	0.1716	6	0.1747

†from ASTM card n 4-0551.

‡vs = very strong, s = strong, ms = medium strong, m = medium, mw = medium weak, w = weak, vw = very weak.

TABLE IV TiO_2 unit-cell volume and phase analysis for undoped TiO_2 and TRh samples heated in a hydrogen stream at 1043 K 5 h

Samples	V (nm^3)	Phases
TiO_2	0.062419	Rutile
TRh 0.7 A*	0.062434	Rutile
TRh 1B*	0.062447	Rutile
TRh 8B*	–	Rutile, Rh

heated for 3 h showed that Rh_2O_3 was in the hexagonal modification, whereas that of the sample heated for 48 h contained the orthorhombic form. In addition, annealing the orthorhombic sample at 973 K in air for 48 h produced no effect.

Table IV lists the X-ray diffraction results obtained for samples heated in H_2 at 1023 K for 5 h. Whereas for undoped TiO_2 this thermal treatment has no effect on the unit-cell volume, for the TRh samples a volume decrease is observed. In addition, metallic rhodium reflections are detected for the sample TRh 8 B*.

3.2. Thermogravimetric measurements

Fig. 1 shows the thermogravimetric curves obtained in hydrogen atmosphere for samples of Series A. A similar behaviour was shown by the specimens of Series B. For the TRh samples two weight-losses are present in the temperature ranges 423 to 623 and 623 to 993 K. For temperatures higher than 1023 K, both for undoped TiO_2 and for the TRh samples, a slight and continuous decrease in weight is observed. The weight changes (%) observed in the temperature range 423 to 993 K, $\Delta(423-993)$, and those taking place in the range 423 to 623 K, $\Delta(423-623)$, are collected in Table I. Fig. 2 shows the rhodium average oxidation number, $\bar{n}$, plotted against the total rhodium content. For each sample the value of $\bar{n}$ was evaluated by considering $\Delta(423-993)$, and the total rhodium content, $[\mathrm{Rh}]_{\mathrm{tot}}$ (expressed as a weight per cent) according to the equation

$$\bar{n} = \frac{\Delta(423-993)}{[\mathrm{Rh}]_{\mathrm{tot}}} \times \frac{102.905}{16/2}, \qquad (1)$$

where 102.905 and 16 are the atomic weights of rhodium and oxygen respectively. The samples of Series A and B show the same behaviour; the $\bar{n}$ values tend to decrease as the total rhodium content increases (see Fig. 2). A thermogravimetric experiment, performed on pure Rh_2O_3 in a hydrogen atmosphere, showed that the rhodium oxide is completely reduced to metallic rhodium by hydrogen in the temperature range 423–623 K.

3.3. ESR spectra

At 77 K a rather complex spectrum is shown by the TRh samples. Fig. 3 shows a series of spectra for samples with increasing rhodium content. At 4.2 K no important variations in the spectral features occur, but at room temperature some components of the spectrum disappear leaving a simpler 3-g value spectrum which is to some extent broadened. This fact, and others that will be discussed below, indicate that the spectrum recorded at low temperatures (77 and 4.2 K) is due to two distinct paramagnetic centres. We call these two centres and their associated signals α and β, β being the signal also observed at room temperature. For the more diluted samples, and at 77 K, each component of the β signal shows an additional splitting due to the hyperfine interaction with the ^{103}Rh

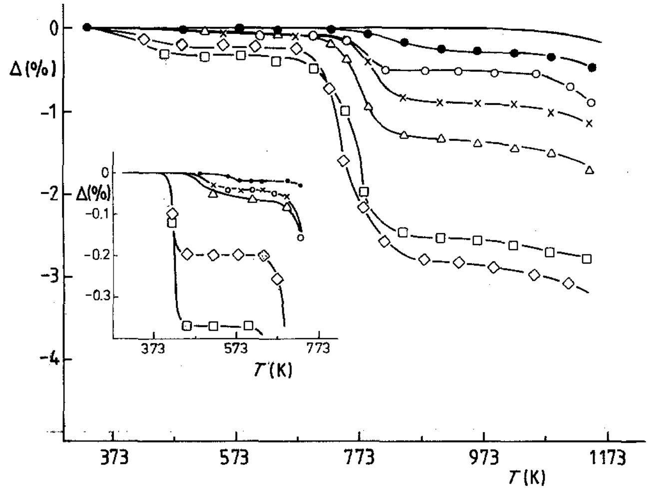

Figure 1 Thermogravimetric curve performed in a hydrogen atmosphere for the TRh A samples. —— TiO_2, ● TRh 0.7 A, ○ TRh 1.5 A, × TRh 3 A, △ TRh 4.5 A, □ TRh 9.5 A, ◇ TRh 11 A. The insert shows the weight-loss in the temperature range 373 to 773 K with an expanded ordinate scale.

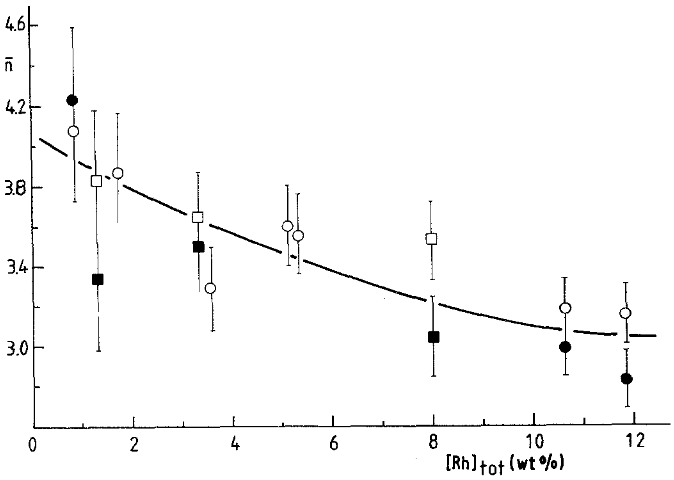

Figure 2 Rhodium average oxidation number, $\bar{n}$, for the TRh samples against the total rhodium content, $[\mathrm{Rh}]_{\mathrm{tot}}$. ○ TRh A series, ● TRh A* series, □ TRh B series, ■ TRh B* series.

nucleus ($I = 1/2$). Table V collects the values of the ESR parameters of these two centres.

The 3-g value signals α and β are typical for $S = 1/2$ ions. Two possible valence states of rhodium giving these signals must be considered: Rh(II), d^7 and Rh(IV), d^5. In octahedral complexes these ions are generally found in low-spin states ($^2E\,(t_2^6e)$ for Rh(II) and $^2T_1\,(t_2^5)$ for Rh(IV)). In the literature a large number of experimental data on ESR spectra of Rh(II) complexes are reported [12–16], but very few on Rh(IV) [15]. Although the principle values of **g** and **A** tensors depend on site symmetry, there are some spectroscopic features of Rh(II) and Rh(IV) complexes which are rather different and can be used for diagnostic purposes. These features, common to the other low-spin d^5 and d^7 ions and well interpreted on theoretical grounds [13], are:

(a) The average **g** value of all low spin d^7 ions is in the range 2.1 to 2.3, whereas that of d^5 ions is 1.7 to 1.9.

(b) The average A_{Rh} for Rh(II) is in the range 0 to 20×10^{-4} cm^{-1} whereas for Rh(IV) it is markedly higher [14].

(c) The Rh(II) spectra can be observed at liquid nitrogen or higher temperatures whereas for Rh(IV) (and its isoelectronic $4d^5$ ions, Ru(III)) [12, 13, 15] liquid helium temperatures are required due to its short relaxation time.

Therefore we assign both signals α and β to Rh(II) ions in solid solution in TiO_2. Moreover, since the spectra recorded at liquid helium temperature do not reveal any new signal we exclude the presence of Rh(IV) in the TRh samples.

The Rh(II) ions give two different signals probable because they can enter into two different sites (i.e. substitutional and/or interstitial). The lack of information on the directions of the principal axes of the **g** tensors, which can be obtained only from a single-crystal study, does not permit direct evidence on the type of the site occupied by the Rh ions to be obtained.

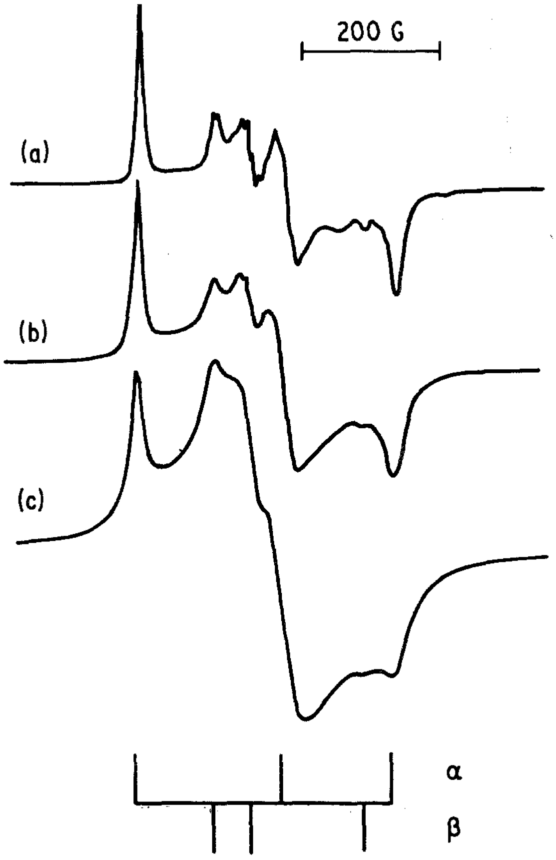

Figure 3 ESR spectra for TRh samples recorded at liquid nitrogen temperature. (a) TRh 0.7 A, (b) TRh 1.5 A, (c) TRh 8 B. For α and β see text.

TABLE V ESR parameters* of the α and β† centres

Centre	g_1	g_2	g_3	g_{av}	A_1 (G)	A_2 (G)	A_3 (G)	A_{av}
α	2.308	2.149	2.042	2.166	‡	–	–	–
β	2.224	2.185	2.064	2.156	6	9	21	12

*Evaluated on spectra recorded at 77 K. Estimated errors ± 0.002 for g values, ± 1 G for A values.
†The same g values are evaluated for β recorded at room temperature.
‡Not resolved.

From the spectra recorded at 77 K in the normal first-derivative presentation it is possible to measure the relative intensity, I_β/I_α, of the signals α and β. The relative intensity I_β/I_α depends largely on the conditions of preparation. With the standard conditions of preparation (firing in air at 1273 K for 5 h) it increases with the rhodium content, passing from about 0.2 for TRh 0.7 A and TRh 1.5 A to about 0.7 for TRh 9.5 A and TRh 11 A. However, there are quite large variations from one preparation to another for the same rhodium content. From the integrated spectra recorded at 77 K we have also determined for the various samples the absolute number of spins, (i.e. the Rh(II) concentration). The results are reported in Fig. 4. Although the reliability of the absolute spin determinations is not high (approximately 40%), due to the large possibility of error in this kind of measurement, the accuracy of their relative values, which is important for the evaluation of the trend of the curve of Fig. 4, is estimated to be within 10%. An important indication is that in all cases the Rh(II), estimated by ESR, is only a small fraction (about 5%) of the rhodium present in solid solution.

The α and β signals are very sensitive to thermal treatments; a study of their reactivity is in progress and will be published separately.

4. Discussion

The results show that rhodium is present in the samples both as Rh_2O_3 and in solid solution in the TiO_2 structure. The presence of the rhodium sesquioxide is directly shown by the phase analysis (Table II) and is confirmed by thermogravimetric measurements. In fact, a loss in weight is observed in the thermogravimetric determinations performed in hydrogen in the same temperature range (423 to 623 K) where the reduction of Rh_2O_3 to metal takes place.

It must be observed that in the present case the thermogravimetric method has a higher sensitivity in detecting Rh_2O_3 than the X-ray diffraction technique. In fact the weight change in the temperature range 423 to 623 K indicates that Rh_2O_3 is present even in some of the more diluted samples (see inset of Fig. 1) whose X-ray spectra do not show Rh_2O_3 lines. In addition, from the thermogravimetric measurements it has been possible to

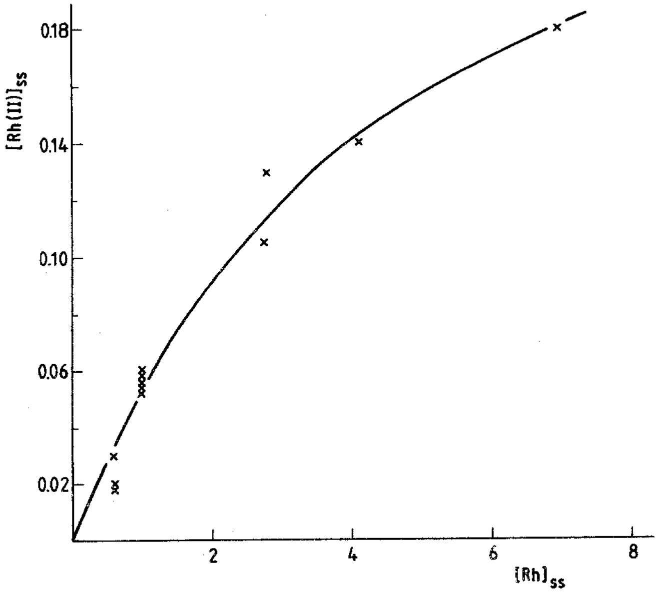

Figure 4 Concentration of Rh(II) in solid solution, $[Rh(II)]_{ss}$, obtained from ESR measurements against the rhodium concentration in solid solution, $[Rh]_{ss}$. The concentrations are expressed as rhodium atoms per 100 titanium atoms.

determine the amount of rhodium present as Rh_2O_3 (Table I).

On the other hand, rhodium incorporation in the rutile structure is clearly shown by the variation of the TiO_2 unit-cell parameter, a, and axial ratio, C, (Table II) and is confirmed by the thermogravimetric measurements. Indeed, the change in weight in the temperature range 673 to 993 K recorded when the TRh samples are heated in hydrogen is explained mainly by the release of oxygen accompanying the reduction of the incorporated species to metal. The metallic rhodium formed segregates out from the TiO_2 structure.

These conclusions are clearly demonstrated by the decrease of the TiO_2 unit-cell volume observed for the TRh samples heated at 1023 K in hydrogen for 5 h (Table IV). At this temperature the reduction of the incorporated species and the segregation of the metal has taken place, and the cause of the TiO_2 unit-cell expansion removed. Furthermore, the reduction of the incorporated rhodium ions to metal is directly shown by the presence of metallic rhodium reflections on the diffraction spectra of the sample TRh 8 B*, heated in hydrogen at 1023 K. As Tables I and II show, this sample does not contain Rh_2O_3 as a separate phase before the hydrogen treatment. On the other hand, the absence of rhodium reflections in the X-ray diffraction spectra of more diluted samples, heated in hydrogen at 1023 K (Table IV) may be accounted for on the basis of the dispersion of the metal on the support. Indeed, in the case of TRh 1 B* a surface area of $10^3\,m^2$ per kg has been measured. For a uniform dispersion as a film of rhodium on the surface, the metal thickness, t, is given by

$$t = \frac{\text{Rh weight/Rh density}}{\text{Sample surface area}}$$

$$= \frac{0.0131}{12.4 \times 10^3(\text{kg m}^{-3})\ 1 \times 10^3(\text{m}^2\ \text{kg}^{-1})} 10^9$$

$$= 1.06\ \text{nm}, \qquad (2)$$

where 0.0131 is the rhodium weight fraction, $12.4 \times 10^3\ \text{kg m}^{-3}$ is the rhodium density [17] and $1 \times 10^3\ \text{m}^2\ \text{kg}^{-1}$ the sample surface area. Although the metal is more likely to be dispersed as particles rather than as a continuous film, it can be understood that the particle size remains below that giving rise to measurable X-ray reflections. In addition, as will be discussed below, the existence of a strong interaction between the metal and the support makes the dispersion highly probable.

As far as the oxidation state of the incorporated species is concerned, it must be recalled that RhO_2 has a rutile-type structure and has been reported to be stable in air up to 953 K [5]. Therefore, since the incorporation in a host matrix tends to stabilize further the oxidation state of the guest species, as shown in the case of Mn(IV), in TiO_2 [7], the incorporation of rhodium in the 4 + oxidation state was considered first. The data of Fig. 2 seemed to support this idea, especially for diluted specimens for which an average oxidation number, $\bar{n}$, close to 4 was found.

Nevertheless, the incorporated rhodium species is not in the 4 + oxidation state but is present in solid solution in TiO_2 as Rh(III). This conclusion is based on several pieces of evidence. Firstly, the expansion of the TiO_2 unit-cell volume (Table II) is not justified on the basis of the Rh(IV) ionic radius. Indeed, according to Shannon [6], $r_{\text{Rh(IV)}} = 0.060$ nm is very close to the value reported for Ti(IV), $r_{\text{Ti(IV)}} = 0.0605$ nm, and no expansion should be expected. Secondly, no Rh(IV) signals are detected by ESR measurements for dilute specimens, even at liquid He temperature. In the ESR spectra, signals due to Rh(II) have been detected instead, but the Rh(II) present was only a small fraction of the total and cannot account for the expansion of the TiO_2 unit-cell volume (see below). Therefore the major part of rhodium must be present in a non-magnetic state, as occurs in Rh(III), a d^6 ion in the low-spin configuration.

On the other hand, the behaviour of the average oxidation number $\bar{n}$, with the rhodium content (Fig. 2) may be explained on the basis of a strong metal–support interaction. As first shown by Tauster [1] the Group VIII metals supported on titanium dioxide may have a peculiar behaviour with respect to the H_2 and CO adsorption capacity; when pre-treated in H_2 at 723 K they show very little H_2 adsorption. The phenomenon has been explained with the possibility of bonding between the noble metal and a titanium entity of the surface. This titanium centre is obtained by reduction of the support, as shown in the case of Pt/TiO_2 by electron microscopy [18]. Therefore, the loss in weight measured in the temperature range 673 to 993 K is not *only* due to the reduction of the incorporated species but also to the reduction of the TiO_2 on the surface of which the metal is

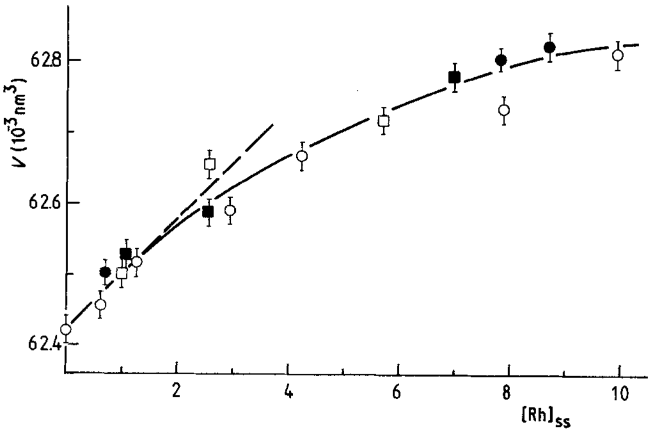

Figure 5 Variation of the TiO_2 unit-cell volume, V, with the rhodium concentration in solid solution, $[Rh]_{ss}$; The concentration is expressed as rhodium atoms per 100 titanium atoms.

supported. As a consequence, when the total decrease in weight, Δ(423–993), is used to evaluate $\bar{n}$, a higher value must be found.

The data show that the effect does not depend on the time of the thermal treatment and is higher for diluted specimens. The latter point may be easily understood by recalling that the samples have a low surface area and as shown before in the case of TRh 1 B* amounts of rhodium up to approximately 1% may interact with the surface. Therefore, only for diluted specimens may the weight change be affected in a substantial manner.

The incorporation of rhodium mainly in the 3 + oxidation state is supported by the variation of the TiO_2 unit-cell volume as the rhodium concentration in solid solution, $[Rh]_{ss}$, (Rh(III) and a small fraction of Rh(II)) has been obtained by subtracting from the total rhodium content the rhodium present in the separate phase, Rh_2O_3, evaluated thermogravimetrically. According to Shannon [6] $r_{Rh(III)} = 0.0665$ nm and an expansion of the TiO_2 unit-cell volume is expected. From the initial linear behaviour, Fig. 5, a variation of V caused by the incorporation of 1% atomic rhodium, $\Delta V_{1\%}$, equal to 0.83×10^{-4} nm^3 is derived. This experimental value is a little higher than that estimated by the appliction of the elastic matrix model. It has been shown [19] that the relationship

$$\Delta V_{1\%}^{calc} = K(r_i^3 - r_{Ti(IV)}^3), \qquad (3)$$

where $K \simeq 1$, and r_i is the ionic radius of the host species, exists between the change of the TiO_2 unit-cell volume, caused by the incorporation of 1% atomic guest ion, and the difference of the ionic radius cubes of the involved species. In fact, by substituting the appropriate values, $\Delta V_{1\%}^{calc} = (0.0665^3 - 0.0605^3)\,nm^3 = 0.73 \times 10^{-4}\,nm^3$ is obtained. Indeed, a higher experimental value is to be expected since, as found by ESR, a small amount of Rh(II) is present in the TiO_2 structure.

A final comment is in order concerning the non-linear variation of V with $[Rh]_{ss}$, see Fig. 5. Two causes may be invoked to explain this behaviour. Firstly the presence of Rh(II) in solid solution: as deduced from Fig. 4, the ratio $[Rh(II)]/[Rh]_{ss}$ decreases as the Rh_{ss} content increases and, therefore, a lower expansion in the TiO_2 unit-cell volume must be found compared to that expected if the ratio were constant. Secondly, the incorporation in TiO_2 of species with oxidation state lower than 4 + induces deviation from the stoichiometry. Shear planes may be formed, a change in the elastic properties of the matrix may thus be expected and the expansion, caused by the increasing concentration of the guest ions, may be different than in the case of more diluted specimens.

References

1. S. J. TAUSTER, S. C. FUNG and R. L. GARTER, *J. Amer. Chem. Soc.* **100** (1979) 170.
2. P. GAYARDO, E. F. GLEASON, J. R. KATZER and A. W. SLEIGHT, Preprints of the 7th International Congress on Catalysis, Tokyo, July 1980, paper E1.
3. P. MERIDIEAU, H. ELLESTAD and C. NACCACHE, Preprints of the 7th International Congress on Catalysis, Tokyo, July 1980, paper E2.
4. L. L. MUREL and D. J. C. YATES, Preprints of the 7th Internation Congress on Catalysis, Tokyo, July 1980, paper E5.
5. O. MULLER and R. ROY, *J. Less-Common Met.* **16** (1968) 129.
6. R. D. SHANNON, *Acta Cryst.* **A32** (1976) 751.
7. M. VALIGI and A. CIMINO, *J. Solid State Chem.* **12** (1975) 135.
8. T. J. WALSH and E. A. HAUSMAN, in "Treatise on Analytical Chemistry" part II, Vol. 8 (Wiley Interscience Publishers, New York and London, 1963) pp. 488, 511.

9. G. LUND, *Z. Anorg. Chem.* **163** (1927) 345.
10. J. M. D. COEY, *Acta Cryst.* **B26** (1970) 1876.
11. A. WOLD, R. J. ARNOTT and W. J. CROFT, *Inorg. Chem.* **2** (1963) 972.
12. J. W. ORTON, "Electron Paramagnetic Resonances", (Iliffe Books, London, 1968) pp. 209, 210.
13. A. ABRAGAM and B. BLEANEY, "Electron Paramagnetic Resonance of Transition Ions" (Clarendon Press, Oxford, 1970) pp. 481–487.
14. A. RAIZMANN, J. T. SUSS and S. SZAPIRO, *Phys. Lett.* **32A** (1970) 30.
15. A. RAIZMANN and J. T. SUSS, Proceeding of the 18th AMPERE Congress, Nottingham, 1974 (North Holland, Amsterdam, 1975) p. 121.
16. G. C. ABELL and R. C. BOWMAN, Jr., *J. Chem. Phys.* **70** (1979) 2611.
17. Handbook of Chemistry and Physics. 49th edition (The Chemical Rubber Co. 1968) p. B.238.
18. R. T. K. BAKER, E. B. PRESTRIDGE and R. L. GARTEN, *J. Catal.* **56** (1979) 390.
19. M. VALIGI and D. GAZZOLI, *Z. Phys. Chem. N.F.* **125** (1981) 89.

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