

## EXAFS EVIDENCE FOR DIRECT Rh-Ta<sup>n+</sup> BONDING AND COVERAGE OF THE METAL PARTICLES IN A Rh/Ta<sub>2</sub>O<sub>5</sub> SMSI CATALYST

J.H.A. MARTENS \*, R. PRINS <sup>+</sup> and D.C. KONINGSBERGER \*

\* *Laboratory for Inorganic Chemistry and Catalysis, Eindhoven University of Technology, P.O. Box 513, NL-5600 MB Eindhoven, The Netherlands*

<sup>+</sup> *Technisch-Chemisches Laboratorium, Eidgenössische Technische Hochschule, CH-8092 Zürich, Switzerland*

Received 18 December 1988; accepted 6 March 1989

An EXAFS investigation showed that the rhodium particles in a Rh/Ta<sub>2</sub>O<sub>5</sub> catalyst were fully reduced and in the 'normal' state after reduction in H<sub>2</sub> at 523 K. After reduction at 858 K, in the SMSI state, tantalum ions could be detected in the reduced supporting oxide directly underneath the rhodium metal particles and in tantalum oxide covering the rhodium metal particles. Neither alloy formation, nor the formation of raftlike structures was observed.

### 1. Introduction

In two recent studies we reported on the structure of a titania supported rhodium catalyst in the normal and the strong metal support interaction (SMSI) state [1,2]. From these studies it became evident that during reduction up to 723 K alloy formation (which is one of the proposed explanations for SMSI) had not taken place. Although coverage of the metal particles by reduced support species was not observed, it could not be completely excluded either. The EXAFS after oxygen adsorption showed that oxidation was suppressed, although the metal particles were covered with adsorbed oxygen [2]. A Rh/Al<sub>2</sub>O<sub>3</sub> catalyst was oxidized under these conditions [2,3]. Thus, if the metal particles in the Rh/TiO<sub>2</sub> sample in ref. [2] were covered with a TiO<sub>x</sub> suboxide, this coverage was not complete.

Recently Logan et al. observed by TEM that rhodium crystallites on TiO<sub>2</sub> were covered with an amorphous TiO<sub>x</sub> deposit after H<sub>2</sub> treatment at 773 K [4]. The amorphous layer appeared to encapsulate the Rh crystallites. These results are in full agreement with our EXAFS results when it is assumed that at 723 K the coverage by the amorphous layer is loose. At higher reduction temperature full coverage will be reached and eventually even a crystalline, adhering TiO<sub>x</sub> overlayer may be formed.

To check this latter possibility we have made an EXAFS study of a Rh/Ta<sub>2</sub>O<sub>5</sub> catalyst reduced at 858 K. We choose Ta<sub>2</sub>O<sub>5</sub> because it is known to be an SMSI support [5] and, more importantly, because tantalum has a backscattering amplitude at higher  $k$ -values which is higher by a factor 2 to 4 than that of titanium [6]. If Ti or Ta atoms are present at short distances from Rh atoms in the SMSI state, we may expect that it will be easier to detect such contributions in Rh/Ta<sub>2</sub>O<sub>5</sub> than in Rh/TiO<sub>2</sub>.

## 2. Experimental

A high surface area Ta<sub>2</sub>O<sub>5</sub> support was prepared by hydrolysis of an acidified aqueous solution of TaCl<sub>5</sub> with ammonia. After filtration, drying and calcination for 1 hr at 873 K the resulting Ta<sub>2</sub>O<sub>5</sub> had a surface area of 100 m<sup>2</sup>g<sup>-1</sup>. From this support a 3 wt% Rh/Ta<sub>2</sub>O<sub>5</sub> catalyst was prepared using the urea method [7]. The resulting sample was dried, calcined at 923 K, pre-reduced in hydrogen at 773 K and oxidized at 573 K. This sample was stored for further use. Temperature programmed reduction experiments indicated that reduction was complete at 470 K when using 4% H<sub>2</sub> in N<sub>2</sub>. Hydrogen chemisorption measurements after reduction at 523, 773 and 873 K gave H/Rh values of 0.93, 0.14 and 0.06, respectively.

The stored Rh/Ta<sub>2</sub>O<sub>5</sub> catalyst was pressed into a thin self supporting wafer, whose thickness was such that  $\mu x = 2.5$  at the rhodium K-edge. The wafer was mounted in an EXAFS cell which enabled in situ pretreatments. All EXAFS spectra were recorded at 100 K at the synchrotron radiation source (SRS) in Daresbury, U.K.

## 3. Results

The backscattering amplitudes  $F(k)$  and the phase shift functions  $\phi(k)$  which are necessary for analyzing the EXAFS data have been obtained from the reference compounds Rh<sub>2</sub>O<sub>3</sub> (for the Rh-O contribution), RhCl<sub>3</sub> (for Rh-Cl), Ta powder (Ta-Ta) and TaCl<sub>5</sub> (Ta-Cl).  $F_{\text{Rh-Ta}} = F_{\text{Ta-Ta}}$  was taken from the L<sub>III</sub> EXAFS spectrum of tantalum powder, while  $\phi_{\text{Rh-Ta}}$  had to be taken from  $\phi_{\text{Rh-Ta}} = \phi_{\text{Rh-Cl}} + \phi_{\text{Ta-Ta}} - \phi_{\text{Ta-Cl}}$  (c.f. ref. [8]), because it could not be obtained from the EXAFS spectrum of the Rh<sub>3</sub>Ta alloy, because of complete overlap of the Rh-Rh and Rh-Ta peaks.

Our procedure for analyzing the EXAFS spectra has been presented before [2,9]. In this procedure EXAFS spectra containing several shells are calculated by using the backscattering amplitudes  $F(k)$  and the phase shift functions  $\phi(k)$  of suitable reference compounds. By varying the coordination number  $N$ , the coordination distance  $R$ , the Debye-Waller factor  $\Delta\sigma^2$  and  $E_0$ , the correction on

Table 1  
Final results from EXAFS data analysis

Treatment	NN	Coordination number		Distance (Å)		$\Delta\sigma^2$ ( $10^{-3} \text{Å}^{-2}$ )	
		(a)	(a)	(a)	(a)	(a)	(a)
R523	Rh	7.9	0.2	2.658	0.005	7.4	1
R858	Rh	7.9	0.2	2.650	0.005	7.0	1
	Ta	1.6	0.5	1.7	0.3	5.4	2
	Ta	0.8	0.2	2.0	0.1	5.4	2

R: reduction in H<sub>2</sub> at 523 or 858 K, NN: nearest neighbour, (a): estimated overall (experimental + systematic) error.

the edge position, the calculated EXAFS spectra are fitted to the measured spectra as accurately as possible. Because of overlapping Rh-Rh and Rh-Ta contributions in the Fourier transform (see fig. 2f), it was impossible to use the difference file technique [2,9]. Instead, a single step multiple shell analysis was used. Because of the high-*Z* character of the main contributions (Rh and Ta), the use of  $k^3$ -weighted Fourier transforms was essential. The results of the analysis procedure are presented in table 1.

In fig. 1a, the raw EXAFS data for the sample reduced in pure H<sub>2</sub> at 523 K for 1 h and the calculated best fitting Rh-Rh EXAFS function are shown. The imaginary parts of the Fourier transforms of these EXAFS functions are shown

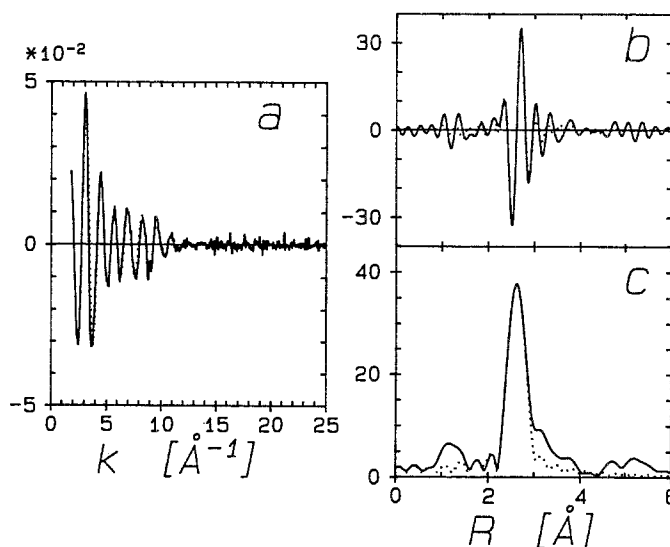


Fig. 1. Rh/Ta<sub>2</sub>O<sub>5</sub> after reduction at 523 K. (a) Raw data (solid line) and calculated Rh-Rh EXAFS function (dotted line), (b) Imaginary parts of the  $k^3$ -weighted Fourier transforms of the raw data (solid line) and calculated Rh-Rh EXAFS function (dotted line), (c) Magnitudes of the  $k^3$ -weighted Fourier transforms of the raw data (solid line) and calculated Rh-Rh EXAFS function (dotted line)

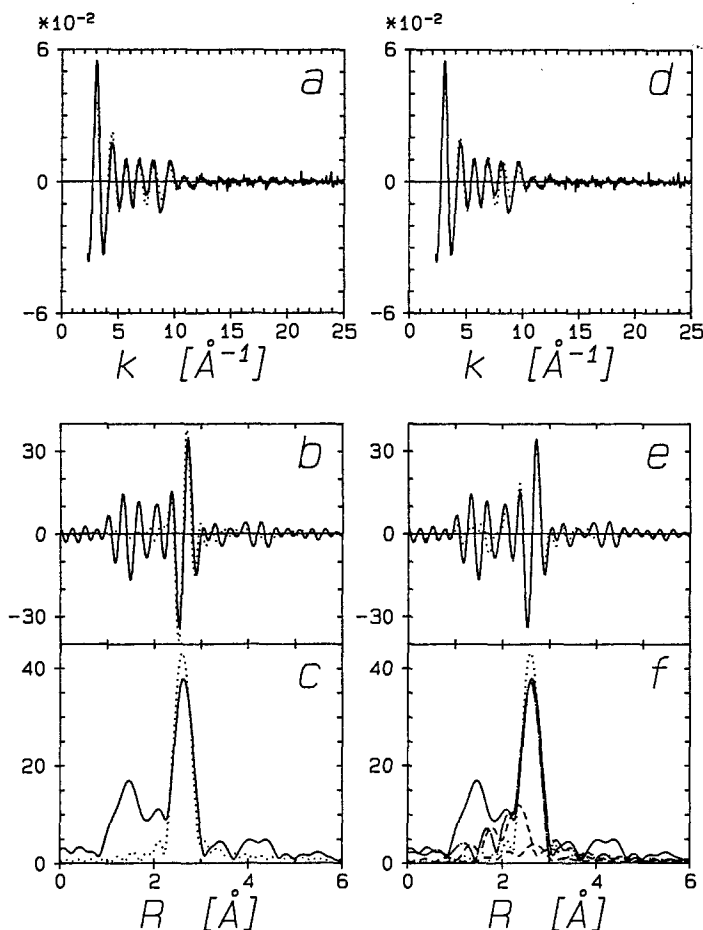


Fig. 2. Rh/Ta<sub>2</sub>O<sub>5</sub> after reduction at 858 K. (a) Raw data (solid line) and calculated Rh-Rh EXAFS function (dotted line), (b) Imaginary parts of the  $k^3$ -weighted Fourier transforms of the raw data (solid line) and calculated Rh-Rh EXAFS function (dotted line), (c) Magnitudes of the  $k^3$ -weighted Fourier transforms of the raw data (solid line) and calculated Rh-Rh EXAFS function (dotted line), (d) Raw data (solid line) and calculated Rh-(Rh+Ta) EXAFS function (dotted line), (e) Imaginary parts of the  $k^3$ -weighted Fourier transforms of the raw data (solid line) and calculated Rh-(Rh+Ta) EXAFS function (dotted line), (f) Magnitudes of the  $k^3$ -weighted Fourier transforms of the raw data (solid line), calculated Rh-Rh EXAFS function (dotted line), the calculated Rh-Ta EXAFS functions (dashed lines) and the sum of the calculated Rh-Rh and Rh-Ta contributions (dash-dotted line)

in fig. 1b and their magnitudes in fig. 1c. Only minor contributions are present next to the Rh-Rh contribution. In fig. 2a the raw EXAFS spectrum and the calculated best fitting Rh-Rh EXAFS function for the sample after a subsequent reduction at 858 K for 15 min are shown. In fig. 2b the imaginary parts of the  $k^3$ -weighted Fourier transforms of the measured data and the calculated Rh-Rh EXAFS function are shown. Figure 2c shows the magnitudes of these Fourier

transforms. The differences in figs. 2b and c at the left hand side of the main Rh-Rh peak are due to neighbouring tantalum ions. We have tried to fit these differences with rhodium and oxygen neighbours, but the fits resulted in physically irrelevant parameters and, furthermore, the best fit was worse than the fit with tantalum neighbours. Figures 2d, e and f show the raw data and the calculated best fitting Rh-(Rh + Ta) EXAFS functions, the imaginary parts of their  $k^3$ -weighted Fourier transforms and the magnitudes of the Fourier transforms of the raw data and of the three separate contributions. Clearly, the agreement at the left hand side of the main Rh-Rh peak in the Fourier transform is better. The Fourier transforms of the EXAFS spectra were complicated by the  $k$ -dependence of  $F(k)$  and  $\phi(k)$ . Therefore, the transforms were corrected for  $F(k)$  and  $\phi(k)$  from rhodium foil, the reference for the Rh-Rh contribution, which was the major contribution in all spectra. As a result, in the Fourier transforms, the Rh-Rh contributions 'peaked' at the correct Rh-Rh distance and the imaginary parts of the Fourier transforms were more or less symmetric.

## 4. Discussion

### 4.1. Rh/Ta<sub>2</sub>O<sub>5</sub> AFTER REDUCTION AT 523 K

According to the TPR experiments, reduction of the sample should be complete at 523 K. Analysis of the EXAFS spectrum confirmed this. Figure 1 shows that apart from a Rh-Rh contribution, only small other contributions were present. From table 1 it can be concluded that on the average each rhodium atom had approximately 7.9 rhodium neighbours at 2.658 Å, which is slightly shorter than the Rh-Rh bulk distance (2.687 Å). From the Rh-Rh coordination number we estimated [10] that the particles were approximately 17 Å in diameter and contained  $73 \pm 5$  rhodium atoms. According to [10], the H/Rh value should be 0.95, which agrees excellently with the measured value, H/Rh = 0.93, and demonstrates that the metal particles were in the 'normal' state. No metal-oxygen contribution from the metal atoms in the metal-support interface, such as reported in [2,9], could be detected. This must be due to the larger size of the metal particles (and thus to a relatively smaller metal-support interface) in the present work.

### 4.2. Rh/Ta<sub>2</sub>O<sub>5</sub> AFTER REDUCTION AT 858 K

After reduction at 773 K, the H/Rh value decreased to 0.14, and after reduction at 873 K to 0.06. Clearly, after reduction at 858 K the metal particles were in the SMSI state. The Rh-Rh coordination number remained unchanged (c.f. table 1). Obviously, the basic structure of the metal particles remained intact. In a study of Pt/TiO<sub>2</sub> it was shown that in the SMSI state the Pt particles were

spread over the support and that ‘pillboxes’ had formed [11]. If such a spread of the metal particles had also occurred in Rh/Ta<sub>2</sub>O<sub>5</sub> it should have been accompanied by a significant decrease in the Rh-Rh coordination number. We did not observe such a decrease and therefore we conclude that in the case of Rh/Ta<sub>2</sub>O<sub>5</sub> spreading of the rhodium particles did not occur. This is in agreement with literature data, indicating that rhodium does not ‘wet’ TiO<sub>x</sub> surfaces [4], like Pt does [11].

Another explanation for SMSI was the formation of alloys [12]. We did not observe contributions from neighbouring tantalum atoms at distances in the range of 2.7–2.8 Å (in the Rh<sub>3</sub>Ta bulk alloy the Rh-Ta distance is 2.729 Å). Therefore, alloy formation can be ruled out in our system. In three other EXAFS studies the observation of an alloy in the SMSI state has been claimed [13–15]. However, we think that the presence of the carbon support might have greatly influenced PtTi alloy formation in the system Pt-TiO<sub>2</sub>/C [13], while the assignment of a peak in the EXAFS spectrum of Rh/TiO<sub>2</sub> to a Rh-Ti alloy contribution [14] is highly questionable because of the applied analysis procedure [2]. The claim of Ni-Nb and Ni-Ti alloy contributions in the EXAFS spectra of Ni/Nb<sub>2</sub>O<sub>5</sub> and Ni/TiO<sub>2</sub> [15], respectively, seems even more questionable because of the extremely narrow window used in the reverse Fourier transformation and because of the fact that others have found that a large fraction of the Ni ions in such systems is not reduced at all, but forms a Ni-Ti-O compound [16]. In our opinion therefore, no unequivocal EXAFS proof for the existence of an alloyed phase in the SMSI state of a M/TiO<sub>2</sub> (or related) system has been presented yet.

In the EXAFS spectrum of the sample after reduction at high temperature, two more contributions were present which both originated from tantalum neighbours at notably short distances. In the Fourier transforms the peaks from both Rh-Ta contributions (at 1.7 and 2.1 Å) overlapped to a large extent with the major Rh-Rh contribution. Furthermore, there was an irregularity around  $k = 9 \text{ \AA}^{-1}$  which gave rise to a peak in the Fourier transform around 1.6 Å. The 1.7 Å Rh-Ta contribution had a main peak at 2.3–2.4 Å in the Fourier transform (shifted from the real Rh-Ta distance, because the Fourier transform was corrected for the Rh-Rh phase shift and backscattering amplitude) and two sidelobes at 1.8 and 1.4 Å (see fig. 2f). The two sidelobes interfered with the artefact at 1.6 Å and thus only the main peak of this Rh-Ta contribution could be used to determine the accompanying parameters. This caused an extra uncertainty in the parameters for the 1.7 Å Rh-Ta contribution.

In table 1 all parameters and their final uncertainties are summarized. Although the uncertainties in the two Rh-Ta parameters are quite large, there is no doubt that tantalum ions are present at distances between 1.4 and 2.1 Å. These are very short coordination distances and can arise only from Ta<sup>n+</sup> ions in direct contact with rhodium atoms in the metal-tantalum (sub)oxide interface. These ions may be located directly underneath the rhodium metal particles. This indicates that indeed the Ta<sub>2</sub>O<sub>5</sub> support under the metal particles had been

reduced. However, the coordination numbers of the Rh-Ta contributions are rather high. When only the rhodium atoms in the metal-support interface have Ta<sup>n+</sup> neighbours, and the support does not expose a large amount of bare Ta<sup>n+</sup> ions, these coordination numbers cannot exceed 0.3 (in the 73 atom metal particle, about 30% of the metal atoms is in the metal-support interface and we assumed that each interfacial rhodium atom can have only one tantalum neighbour at such a short distance). Therefore, we conclude that also the rhodium surface atoms, which are not in the metal-support interface, must be in direct contact with Ta<sup>n+</sup> ions and that the metal particles were substantially covered with reduced Ta<sub>2</sub>O<sub>5</sub>. The direct contact between rhodium atoms and tantalum ions after reduction at high temperature could result in a strong interaction between metal particle and support.

In the Rh/TiO<sub>2</sub> samples we did not directly observe covering, but we could not exclude partial covering either [2]. The fact that the rhodium metal particles in Rh/Ta<sub>2</sub>O<sub>5</sub> are covered to a larger extent than the metal particles in Rh/TiO<sub>2</sub> can be explained in several ways. First of all, the metal particles in Rh/TiO<sub>2</sub> are very small [1,2] and coverage has up to now only been reported in literature for larger metal particles. Another reason might be the fact that the Rh/Ta<sub>2</sub>O<sub>5</sub> sample was reduced at a much higher temperature (858 K) than the Rh/TiO<sub>2</sub> samples (723 and 773 K). A third reason may be that the Rh/TiO<sub>2</sub> samples were prepared by exchanging with a solution of Rh(NO<sub>3</sub>)<sub>3</sub> which had a relatively high pH. The Rh/Ta<sub>2</sub>O<sub>5</sub> sample was prepared using the urea method and therefore, the starting pH was low. Thus, during the preparation of the Rh/Ta<sub>2</sub>O<sub>5</sub> sample, some Ta<sub>2</sub>O<sub>5</sub> might have dissolved and later precipitated on top of the rhodium metal particles. This kind of coverage has already been reported for Rh/V<sub>2</sub>O<sub>3</sub> by Van der Lee et al. [17]. After reduction at high temperature, this Ta<sub>2</sub>O<sub>5</sub> on top of the metal particles will become reduced and may have an intimate contact with the metal particle, giving rise to Rh-Ta<sup>n+</sup> bonding.

### Acknowledgements

This study was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO). The authors acknowledge the skillful assistance of the Daresbury SRS staff and the invaluable assistance of F.W.H. Kampers, F.B.M. van Zon and J. van Grondelle of the Eindhoven University during the EXAFS measurements.

### References

- [1] D.C. Koningsberger, J.H.A. Martens, R. Prins, D.R. Short and D.E. Sayers, *J. Phys. Chem.* 90 (1986) 3047.

- [2] J.H.A. Martens, R. Prins, H. Zandbergen and D.C. Koningsberger, *J. Phys. Chem.* 92 (1988) 1903.
- [3] J.H.A. Martens, R. Prins and D.C. Koningsberger, *J. Phys. Chem.*, to be published.
- [4] A.D. Logan, E.J. Braunschweig, A.K. Datye and D.J. Smith, *Langmuir* 4 (1988) 827.
- [5] S.J. Tauster and S.C. Fung, *J. Catal.* 55 (1978) 29.
- [6] B.K. Teo and P.A. Lee, *J. Am. Chem. Soc.* 101 (1979) 2815.
- [7] J.W. Geus, in: *Preparation of Catalysts*, eds. G. Poncelet, P. Grange and P.A. Jacobs, Vol. III (Elsevier, Amsterdam, 1983) p. 1.
- [8] J.H. Sinfelt, G.H. Via, F.W. Lytle and R.B. Gregor, *J. Chem. Phys.* 72 (1980) 4832.
- [9] J.B.A.D. van Zon, D.C. Koningsberger, H.F.J. van 't Blik and D.E. Sayers, *J. Chem. Phys.* 82 (1985) 5742.
- [10] B.J. Kip, F.B.M. Duivenvoorden, D.C. Koningsberger and R. Prins, *J. Catal.* 105 (1987) 26.
- [11] R.T.K. Baker, E.B. Prestridge and R.L. Garten, *J. Catal.* 56 (1979) 390.
- [12] S.J. Tauster, S.C. Fung and R.L. Garten, *J. Am. Chem. Soc.* 100 (1978) 170.
- [13] B.C. Beard and P.N. Ross, *J. Phys. Chem.* 90 (1984) 6811.
- [14] S. Sakellson, M. McMillan and G.L. Haller, *J. Phys. Chem.* 90 (1986) 1733.
- [15] G. Sankar, S. Vasudevan and C.N.R. Rao, *J. Phys. Chem.* 92 (1988) 1878.
- [16] H.C. zur Loye and A.M. Stacey, *J. Am. Chem. Soc.* 107 (1985) 4567.
- [17] G. van der Lee, B. Schuller, H. Post, T.L.F. Favre and V. Ponc, *J. Catal.* 98 (1986) 522.