EXAFS EVIDENCE FOR DIRECT Rh-Ta"+ BONDING AND COVERAGE OF THE METAL PARTICLES IN A Rh/Ta₂O₅ SMSI CATALYST

J.H.A. MARTENS *, R. PRINS + and D.C. KONINGSBERGER *

* Laboratory for Inorganic Chemistry and Catalysis, Eindhoven University of Technology, P.O. Box 513, NL-5600 MB Eindhoven, The Netherlands
+ 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/Ta₂O₅ catalyst were fully reduced and in the 'normal' state after reduction in H₂ 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/Al₂O₃ catalyst was oxidized under these conditions [2,3]. Thus, if the metal particles in the Rh/TiO₂ sample in ref. [2] were covered with a TiOₓ suboxide, this coverage was not complete.

Recently Logan et al. observed by TEM that rhodium crystallites on TiO₂ were covered with an amorphous TiOₓ deposit after H₂ 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 TiOₓ overlayer may be formed.
To check this latter possibility we have made an EXAFS study of a Rh/Ta$_2$O$_5$ catalyst reduced at 858 K. We choose Ta$_2$O$_5$ 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$_2$O$_5$ than in Rh/TiO$_2$.

2. Experimental

A high surface area Ta$_2$O$_5$ support was prepared by hydrolysis of an acidified aqueous solution of TaCl$_5$ with ammonia. After filtration, drying and calcination for 1 hr at 873 K the resulting Ta$_2$O$_5$ had a surface area of 100 m$^2$g$^{-1}$. From this support a 3 wt% Rh/Ta$_2$O$_5$ 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$_2$ in N$_2$. 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$_2$O$_5$ 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$_2$O$_3$ (for the Rh-O contribution), RhCl$_3$ (for Rh-Cl), Ta powder (Ta-Ta) and TaCl$_5$ (Ta-Cl). $F_{\text{Rh-Ta}} = F_{\text{Ta-Ta}}$ was taken from the L$_{III}$ 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$_3$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