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Rh-V alloy formation in Rh-VOx thin films after high-temperature reduction studied by electron microscopy

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Abstract

Rh nanoparticles (mean size 10 and 15 nm), prepared by epitaxial growth on NaCl surfaces, were covered with layers of crystalline vanadium oxide (mean thickness 1.5 and 25 nm) by reactive deposition in 10(-2) mbar O-2. The 1.5 nm film was further stabilized with a coating layer of 25 nm amorphous alumina. The so-obtained Rh/vanadia films, containing vanadium in the V3+ and V2+ state, were treated in 1 bar O-2 at 673 K for 1 h and thereafter reduced in 1 bar H-2 at increased temperatures, particularly between 723 and 873 K. The structural and morphological changes were followed by (high-resolution) transmission electron rnicroscopy and selected area diffraction. Oxidation at 673 K transforms the purely vanadia-supported samples into Rh/V2O5, while in the alumina-supported films containing only small amounts of VOx, the formation of topotactic V2O3 is observed. The formation of Rh-V alloys during the subsequent reduction is strongly determined by the intimate contact and the structural and orientational relationship between Rh particles and the surrounding VOx phase. Reduction above 473 K transforms the support into substoichiometric vanadium oxides of composition VO and V2O. Analysis of high-resolution images and diffraction patterns reveals the presence of different alloy phases after reduction with increasing T (from 573 up to 823 K). In the alumina-supported film (low V/Rh ratio) the epitaxial alignment between the Rh particles and the Surrounding V2O3 phase apparently favours the primary formation of defined alloys of type V3Rh and VRh3, followed by VRh at higher temperature. On the contrary, mainly V3Rh5 is formed in the purely VOx- supported Rh/films, clue to different epitaxial relations in the initial state. Possible pathways of alloy formation are discussed.