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 V\(_{3+}\) and V\(_{2+}\) 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 microscopy and selected area diffraction. Oxidation at 673 K transforms the purely vanadia-supported samples into Rh/V\(_2\)O\(_5\), while in the alumina-supported films containing only small amounts of VO\(_x\), the formation of topotactic V\(_2\)O\(_3\) 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 VO\(_x\) phase. Reduction above 473 K transforms the support into substoichiometric vanadium oxides of composition VO and V\(_2\)O. 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 V\(_2\)O\(_3\) phase apparently favours the primary formation of defined alloys of type V\(_3\)Rh and VRh\(_3\), followed by VRh at higher temperature. On the contrary, mainly V\(_3\)Rh\(_5\) is formed in the purely VO\(_x\)-supported Rh/films, due to different epitaxial relations in the initial state. Possible pathways of alloy formation are discussed.