

Oxidation of stepped Rh surfaces: PEEM and XPS studies

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The role of rhodium bulk and surface oxides in catalytic surface reactions is intensively and controversially discussed [1, 2], particularly under aspects of increasing application of Rh in the newest generation of exhaust catalysts [3]. Therefore *in situ* identification of the oxidation state of the Rh based catalysts is crucial for understanding the reaction mechanisms on partially oxidized surfaces. In studies of surface oxidation of Rh most efforts are traditionally focused on low Miller index surfaces, whereas the highly stepped Rh surfaces, mostly present under realistic conditions, are much less studied. Particularly, the anisotropy of the initial oxidation of such surfaces is not adequately explored, despite the evident importance of the issue: differently oriented facets of a catalytic particle may exhibit different chemical states during the reaction. To reveal such anisotropy, surface analysis of crystallographically different Rh surfaces exposed to identical oxidizing conditions is necessary.

A new approach, based on local analysis of individual μm -sized domains of a polycrystalline Rh foil, where each domain is crystallographically characterized by EBSD [4], allows such access, e.g. by spatially resolved XPS or by surface microscopies with chemical resolution, e.g. by PEEM. Since all the domains belong to the same sample, such approach automatically provides identical conditions for each of the differently oriented surface regions. It is also advantageous in comparison to studies on single crystal surfaces, where separate experiments using differently oriented samples are required.

In present contribution, anisotropy of the surface oxidation of stepped (high Miller index) Rh surfaces is studied in the 10^{-5} mbar pressure range of molecular oxygen and in the temperature range of 573 to 773 K by spatially resolved XPS and by PEEM, using the "kinetics by imaging" approach [5]. As a model system, highly stepped, differently oriented, 50-200 μm wide domains of a polycrystalline Rh foil are used. The results are discussed from the standpoint of the catalytic CO and H₂ oxidation reaction on Rh.

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References:

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