Electrochimica Acta 54 (2009) 5023–5029

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Electrochemical surface faceting of Re(11$\bar{2}$1)

Timo Jacob*

Institut für Elektrochemie, Universität Ulm, D-89069 Ulm, Germany

ARTICLE INFO

Article history:
Received 19 December 2008
Received in revised form 2 March 2009
Accepted 5 March 2009
Available online 24 March 2009

Keywords:
Density functional theory
Rhenium
Oxygen
Ammonia
Faceting
Nanostructuring

ABSTRACT

Using density functional theory calculations and the extended *ab initio* atomistic thermodynamics approach, we studied the adsorption of oxygen and nitrogen on Re(11$\bar{2}$1) before and after surface faceting. Constructing the electrochemical surface phase diagrams of Re(11$\bar{2}$1) in contact with an aqueous electrolyte or with ammonia, we find the same surface structures to become thermodynamically stable as observed experimentally under UHV conditions. While at low electrode potentials the planar surfaces are stable, more positive potentials stabilize four-sided nano-facets due to O^{2-} adsorption and two-sided nano-ridges in case of N^{3-} adsorption from the electrolytes.

1. Introduction

Studies of structure sensitivity and selectivity in (electro-) chemical reactions have attracted attention for many years, and the relative roles of particle size effects, the crystallographic structure of surfaces, ensemble effects, etc., have been discussed extensively. To address such issues, innovative new nanofabrication methods for assembling model catalysts at the nanometre-scale have been developed [1]. However, there are relatively few studies on the surface chemistry of nanoscale particles or surface features with specific, well-defined crystal facets and a narrow size distribution [1–6]. One way out of this dilemma is the formation of well-defined nanostructures or facets on single-crystal surfaces [7–9], which provides a reproducible basis and model systems for studying structural sensitivity in (electro-)catalytic reactions [10–12] and may be used as templates to grow nanostructures.

Surface faceting can be understood as a morphology change from a flat bulk-truncated surface to a hill-and-valley structure. While clean surfaces rarely facet, the adsorption of gases or metallic monolayers (MLs) facilitates the faceting of initially planar surfaces with relatively high specific surface free energies [*i.e.*, a surface that is rough on the atomic scale, such as bcc W(1 1 1), fcc Ir(2 1 0) or hcp Re(11$\bar{2}$1)]. Upon heating, nanoscale features terminated by facets nucleate, grow and cover the surface. Usually, the resulting facets are more close-packed than the original planar substrate, and invariably the overall surface energy is reduced by facet formation, even though the surface area increases [13,14].

There is extensive literature that describes how the faceting of initially planar surfaces is facilitated by the adsorption of gases and metallic MLs that enhance the anisotropy of the surface free energy [9]. Besides a few recent studies of faceting induced by metals on metals [13,15,16], there are many papers on the faceting of metals induced by gaseous or other non-metallic impurities, as well as on the faceting of semiconductors under a variety of conditions. Surfaces for which adsorbate-induced faceting has been observed include nanoscale supported catalysts [17–19], vicinal Cu surfaces, O/Ir(2 1 0), O and Cl/W(1 1 1) and O/Mo(1 1 1), O/Re(12$\bar{3}$1), O/Re(11$\bar{2}$1), N/Re(11$\bar{2}$1), N/Fe(1 1 1), Au-covered vicinal Si, Cl/Ag(1 1 1), O/Pt(2 1 0), O/Rh(2 1 0), O/NiAl(1 1 1) and CO and O/Pt(1 1 0) at high pressure, activated nitrogen on Cu(2 1 0) and Ni(2 1 0), and even CO/Ni(1 1 0) at high pressure and temperature (for an overview see Ref. [20] and references therein).

So far, only few theoretical studies have been reported on the overlayer-induced faceting of surfaces [21–25]. These studies in general support the picture that strongly interacting adsorbates enhance the anisotropy in the surface free energy of both planar and faceted surfaces. However, Che et al. [21] argued that a formation barrier to nucleation might in some cases prevent the surface from faceting. Furthermore, facet formation on Ir and Re surfaces induced by oxygen and nitrogen adsorption has been studied on the basis of density functional theory calculations and thermodynamic considerations. While on Ir(2 1 0) the presence of oxygen led to the stabilization of three-sided nanopyramids [10,24,25], on Re(11$\bar{2}$1) and Re(12$\bar{3}$1), a variety of additional structures appeared in the corresponding phase diagrams [26,27]. These ranged from two-sided

* Tel.: +49 731 5025417; fax: +49 731 5025409.
E-mail address: timo.jacob@uni-ulm.de.

0013-4686/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2009.03.033

ridges to four-sided nanopyramids. Since contributions from edges, kinks and/or strain are usually omitted in these calculations, so far, theoretical studies have been limited to systems that show a high enough anisotropy in surface free energy but additionally small edge and kink energies.

For Re, a *hcp* metal, little is known about its faceting behavior, although it is an important component for many catalysts. Re has a higher heat of oxide formation than Ir, Rh or Pt, and the faceting is considerably more complicated. By low energy electron diffraction (LEED) and scanning tunnelling microscopy (STM) under ultra-high vacuum (UHV) conditions the group of Madey observed a complex morphological evolution of faceting on Re(12$\bar{3}$1) and Re(11$\bar{2}$1). When Re(12$\bar{3}$1) is covered with 0.7–0.9 ML oxygen and annealed long ridges emerge exhibiting (01$\bar{1}$0) and (11$\bar{2}$1) faces [28]. For 0.9–1.0 ML, the ridges become truncated by a third face, (10$\bar{1}$0), which has the same surface structure as (0 1 $\bar{1}$ 0) but a higher tilt angle with respect to (12$\bar{3}$1) [28]. When Re(12$\bar{3}$1) is fully covered by oxygen (1 ML), a fourth face (01$\bar{1}$1) also emerges upon annealing (see Fig. 8 in Ref. [20]). It is not surprising that (01$\bar{1}$0), (10$\bar{1}$0) and (01$\bar{1}$1) appear as faces because they all have rather smooth surfaces and thus low surface free energies.

For initially planar Re(11$\bar{2}$1), which is the surface of interest for the present work, UHV studies revealed that the adsorption of oxygen at room temperature, followed by annealing to elevated temperatures, caused the surface to become partially faceted with (01$\bar{1}$0) and (10$\bar{1}$0) faces, forming zig-zag chains (see Fig. 9 in Ref. [20]). Under oxidation conditions, *i.e.* dosing a large amount of oxygen at high temperatures (900–1000 K), the (11$\bar{2}$1) surface became completely covered by four-sided nanoscale pyramidal structures, whose facets were identified as (01$\bar{1}$0), (10$\bar{1}$0), (01$\bar{1}$1) and (10$\bar{1}$1) [26]. In contrast, after exposure to ammonia at 700 K, the Re(11$\bar{2}$1) surface exhibited a (1×2) reconstruction and remained planar (ammonia dissociates on Re, and only N remains on the surface at $T > 600$ K). Upon exposure to ammonia at 900 K, the Re(11$\bar{2}$1) surface became completely faceted, forming two-sided ridge-like structures (see Fig. 10 in Ref. 20); the orientations of the ridge sides were (13$\bar{4}$2) and (31$\bar{4}$2), which were different from any of the facets found in the oxygen-induced faceting of Re(12$\bar{3}$1) and Re(11$\bar{2}$1) [26].

While much work has been reported for surface faceting under UHV conditions, expanding the effect to the electrochemical environment is still in its infant stage. By a combined theoretical and experimental effort, we could recently show that faceting of Ir(2 1 0) is also possible outside a UHV-chamber and that faceted Ir(2 1 0) becomes stabilized even under electrochemical conditions, thus providing a basis for studies on structure sensitivity of electrocatalytic reactions [29]. In continuation of these studies and motivated by the UHV-experiments of the Madey group on Re(11$\bar{2}$1), in the present work we used a combination of density functional theory (DFT) together with the recently formulated extended *ab initio* atomistic thermodynamics to evaluate the electrochemical faceting phase diagrams of Re(11$\bar{2}$1). By assuming either an aqueous or a nitrogen-containing (here ammonia) electrolyte, we will show that by choosing the appropriate electrolyte and electrode potentials surface faceting of Re(11$\bar{2}$1) should also be possible electrochemically, finally allowing to actively change the surface morphology for investigating structure sensitivity in electrocatalysis on well-defined surfaces or as templates for the growth of nanostructures.

2. Methods of calculation

2.1. Facet formation condition

The energy required to form facets can be expressed as a sum of changes in the Gibbs free energies mainly related to surface, edge, kink and strain contributions:

$$\Delta G^{\text{form}} = \Delta G^{\text{surface}} + \Delta G^{\text{edge}} + \Delta G^{\text{kink}} + \Delta G^{\text{strain}} + \cdots. \quad (1)$$

As long as the facets are large enough such that contributions from step-edges, kinks, and strain are negligible compared to surface contributions, the overall formation energy can be approximated by the surface contribution only. This condition is usually referred to as the Herring-condition, which as we could already show for the facet formation on Ir(2 1 0) [29] seems to be suitable for the present system. On the basis of this condition facet formation should occur when

$$\Delta G^{\text{form}} \approx \Delta G^{\text{surface}} = \sum_f A_f^{\text{final}} \gamma_f^{\text{final}} - A^{\text{initial}} \gamma^{\text{initial}} < 0, \quad (2)$$

where the initial surface is characterized by a surface free energy γ^{initial} and an overall surface area A^{initial}, and the fth-face of the facets accordingly by γ_f^{final} and A_f^{final}. Exemplarily for the case where oxygen adsorption induces the formation of four-sided nanopyramids exhibiting Re(10$\bar{1}$0), (01$\bar{1}$0), (10$\bar{1}$1), and (01$\bar{1}$1) faces, Eq. (2) converts into the following condition, which has to be fulfilled in order to show facet formation:

$$\frac{S_{10\bar{1}0}}{\cos \upsilon_{10\bar{1}0}} \cdot \gamma_{10\bar{1}0}(T, a_{H_2O}, \Delta\phi) + \frac{S_{01\bar{1}0}}{\cos \upsilon_{01\bar{1}0}} \cdot \gamma_{01\bar{1}0}(T, a_{H_2O}, \Delta\phi) + \frac{S_{10\bar{1}1}}{\cos \upsilon_{10\bar{1}1}} \cdot \gamma_{10\bar{1}1}(T, a_{H_2O}, \Delta\phi) + \frac{S_{01\bar{1}1}}{\cos \upsilon_{01\bar{1}1}} \cdot \gamma_{01\bar{1}1}(T, a_{H_2O}, \Delta\phi) < \gamma_{11\bar{2}1}(T, a_{H_2O}, \Delta\phi). \quad (3)$$

Here all S_f specify the partial contributions of the different faces to each pyramidal-shaped facet, while all υ_f are the tilt angles of the faces with respect to the initial substrate, T is the temperature, a the water activity, and $\Delta\phi$ the potential difference between electrode and electrolyte. Experimentally and geometrically obtained values for S_f and υ_f are summarized in Table 1. It should be noted that since Re(10$\bar{1}$0) and (01$\bar{1}$0), as well as Re(10$\bar{1}$1) and (01$\bar{1}$1) show the same surface morphologies, respectively, in each case both can be combined.

The interfacial free energies γ, which are relevant for Eq. (3), give the stability of the corresponding electrode/electrolyte-interfaces. As described in Refs. [30,31] an exact evaluation of the interfacial free energies is in principle possible, but requires a self-consistent modeling of the entire interfacial region, which might range up to several 100 Å. Since this is beyond nowadays capabilities of *ab initio* approaches, we reduce our model to the electrode and the adlayer only and assume a constant influence of the electrolyte, allowing us to neglect its presence when studying relative stabilities only. While this represents the extreme case, where only the faceting-inducing species (here oxygen or nitrogen) are present on the surface, further studies will investigate the role of partially dehydrogenated surface species, which might be present at intermediate potentials.

Finally, the interfacial free energy of the electrochemical interface, which was obtained by an extension of the *ab initio* ther-

Table 1
Surface area A (per 1×1-unit cell (calculated)), partial surface contributions (S) and tilt angles (υ) for the initial substrate and two types of nano-facets: two-sided ridges consisting of (13$\bar{4}$2) and (13$\bar{4}$2) faces, and four-sided pyramids consisting of (10$\bar{1}$0), (01$\bar{1}$0), (10$\bar{1}$1), and (01$\bar{1}$1) faces. For S the experimentally measured and geometrically derived values are given.

Surface	A (Å^2)	S^{exp}	S^{geo}	υ^{geo} (°)
Re(11$\bar{2}$1)	22.54	–	–	–
Re(10$\bar{1}$0)/(01$\bar{1}$0)	12.43	0.44 ± 0.02	0.456	34.18
Re(10$\bar{1}$1)/(01$\bar{1}$1)	14.11	0.56 ± 0.02	0.544	29.68
Re(13$\bar{4}$2)/(13$\bar{4}$2)	46.77	1.0	1.0	15.42