Available online at www.sciencedirect.com

ScienceDirect

Electrochimica Acta 53 (2007) 349–361

ELECTROCHIMICA Acta

www.elsevier.com/locate/electacta

Spillover of primary oxides as a dynamic catalytic effect of interactive hypo-d-oxide supports

Jelena M. Jaksic [a,b], Nedeljko V. Krstajic [a], Ljiljana M. Vracar [a], Stelios G. Neophytides [b], Diamantoula Labou [b], Polycarpos Falaras [c], Milan M. Jaksic [a,b,*]

[a] *Faculty of Technology and Metallurgy, University of Belgrade, Belgrade, Serbia*
[b] *Institute of Chemical Engineering and High Temperature Chemical Processes, FORTH, Patras, Greece*
[c] *Institute of Physical Chemistry, NCSR Demokritos, Attikis, Athens, Greece*

Received 16 November 2006; received in revised form 14 June 2007; accepted 14 June 2007

Abstract

The aim of the present paper is to introduce electron conductive and d–d-interactive individual and composite hypo-d-oxides of increased altervalent capacity, or their suboxides (Magneli phases), as catalytic supports and therefrom provide: (i) the Strong Metal-Supports Interaction (SMSI) effect and (ii) dynamic spillover interactive transfer of primary oxides (M–OH) for further electrode reactions and thereby advance the overall electrocatalytic activity. Since hypo-d-oxides feature the exchange membrane properties, the higher the altervalent capacity, the higher the spillover effect. This is the reason why anatase titania has now been doped with a certain amount of colloidal tungstenia (WO_3) ingredient, and the latter individually employed as the interactive catalyst support. Potentiodynamic experiments have shown that the reversible peak of the primary oxide growth on Pt, Ru and Au supported upon hypo-d-oxides and suboxides becomes distinctly increased in the charge capacity and shifted to remarkably more negative potential values, so that it starts even within the range of H-adatoms desorption, while its reduction extends until and merge with the UPD of hydrogen atoms. With wet tungstenia-doped titania-supported Pt catalyst in membrane cells, these peaks dramatically increase in their charge capacity and reversibly become shrunk with decreased moisture content in the feeding inert gas mixture, and *vice versa*. Such distinct potentiodynamic scans in conjunction with some broadened complementary kinetic electrocatalytic improvements, rising from the same hypo-d-oxide and/or suboxide interactive support effects, have been proved to be the best and comparable experimental evidence for the spillover effect of primary oxides.

Keywords: Catalytic spillover; Primary oxide; Surface oxide; Strong Metal-Support d–d-Interaction (SMSI); Hypo-hyper-d–d-interactive bonding; Intermetallic phases; Altervalent capacity

---

1. Introduction

A bridge between heterogeneous catalysis and electrocatalysis has been established when titanium suboxides ($Ti_nO_{(2n-1)}$, in average Ti_4O_7) or Magneli phases [1–3] have been introduced as a rather stable and interactive catalytic support with pronounced metallic type or electronic conductivity ($300–1000\,S\,cm^{-2}$). Even more so, the remarkable step ahead was imposed when it has been shown that monolayers of anatase titania, zirconia, hafnia, tungstenia and their proper mixtures, under specific conditions, in contact with metallic or even oxide type catalyst, feature the same electronic conductivity (no charge separation in XPS analysis) and much larger available surface area, with even more pronounced interactive support properties [1].

1.1. Strong Metal-Support Interaction effect in electrocatalysis

The whole contemporary heterogeneous catalysis is based on supported catalysts, where an individual or prevailingly hyper-d-electronic metal arises in the Strong d–d-Metal-Support Interaction (SMSI) with mostly hypo-d-oxide (TiO_2, ZrO_2, HfO_2) or various hypo-d-hypo-f-oxide supporting composites (TiO_2, CeO_2) [4–7]. Brewer [8–11] hypo-hyper-d–d-interelectronic bonding theory precedes and in its extended interionic bond-

---

[*] Corresponding author at: Institute of Chemical Engineering and High Temperature Chemical Processes, FORTH, Stadiou Road, Platani, GR-26500 Patras, Greece.

E-mail address: Milan@iceht.forth.gr (M.M. Jaksic).

0013-4686/$ – see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2007.06.062

ing model [2,12] *a priori* anticipates the Tauster [4–7] SMSI, so that with such substantially d–d-interactive properties has recently been in addition used for the basis of ordered catalyst grafting (anchoring) upon suitable hypo-d-oxide supports [1,2,12]. In such a context, Tauster and Fung [4–7] intuitively predicted the formation of stable intermetallic phases ($TiPt_3$) at the interphase M/TiO_2, to be decisive for the overall d–d-SMSI effect that has been now experimentally (XPS) confirmed [1,12]. The operational basic Tauster [4–7] definition of SMSI implies that the d–d-metal–oxide interaction (M/TiO_2) for heterogeneous catalysis, in accordance with the bonding strength, results in substantial weakening and even suppression of intermediate chemisorptive bonds (M–H, M–CO). In general, since the d-orbital is both the bonding and adsorptive band [1,2,12,13], the stronger the hypo-hyper-d–d-interelectronic bonding, either intermetallic or interionic, the more strained and more exposed appear d-orbitals, the more strained and more weakened are the metal/adsorptive intermediate ties in the RDS, and thereby further consequently (Sabatier principle in heterogeneous catalysis [14]), the higher the whole synergistic (electro)catalytic effect arises [2,4–7,12–15]. Meanwhile, new concepts additionally imply the spillover of interactive primary oxides (M–OH) [2,12,17,18] and their decisive interference in the overall catalytic process (see downwards). However, while the dynamic spillover effect of the primary oxide (M–OH) dipoles repulsion takes place all over the available metallic surface regardless its nano-sized magnitude, the SMSI effect usually imposes along the circumference of the two phase boundary for larger nanostructured metal/support composite electrocatalysts (M/TiO_2 or $M/(Ti_4O_7)$) and tends to its maximum when metallic deposit takes smaller nano-sizes and approaches monoatomic network dispersion. Following the same rule, the stronger the hypo-hyper-d-interionic metal-oxide support interaction the higher the overall catalytic activity [1,2,12,18].

Since the d-band is both the bonding and chemisorptive orbital with linear interdependence between surface free- and cohesive-energy (in so called “one by six relation”[19]) [16], while the s,p-electrons contribute a constant term to both of them all along the periodic table, there exists almost a linear correlation between the bonding effectiveness and electrocatalytic activity [1,2]. Namely, alike the majority of physical and chemical properties, that feature periodicity within the volcanic plots [16,20] along transition series, including electrocatalysis for the HELR ($\log j_o$ or polarization, η) [21,22], it has been inferred that along each hypo-hyper-d–d-interelectronic phase diagram, there appear the same volcano plots amongst series of various intermetallic phases between the initial constituents, as the part of general dependence between two initial periods of composing metals [1,2,12]. In other words, such intermetallic phases play the role of missing elements between two initial constituents along the periodic table. Such behavior is the consequence of the fact that every hypo-d-electronic element belongs to the ascending, and the hyper-d-metal to the descending part of the general type volcano plots (symmetric and asymmetric) along the transition series [16,20], while their stable intermetallic phases replace the missing elements in between. In such a respect, volcanic plots of the electrocatalytic activity for the HELR and cohesive bonding energy of intermetallic phases are almost overlapping and coincidently similar in their shape (Fig. 1), so that the plot of one into another, results in the straight line (one-to-one linear) dependence, with the slope, that correlates with the constant in the Langmuir adsorption isotherm for H-adatoms. Since the

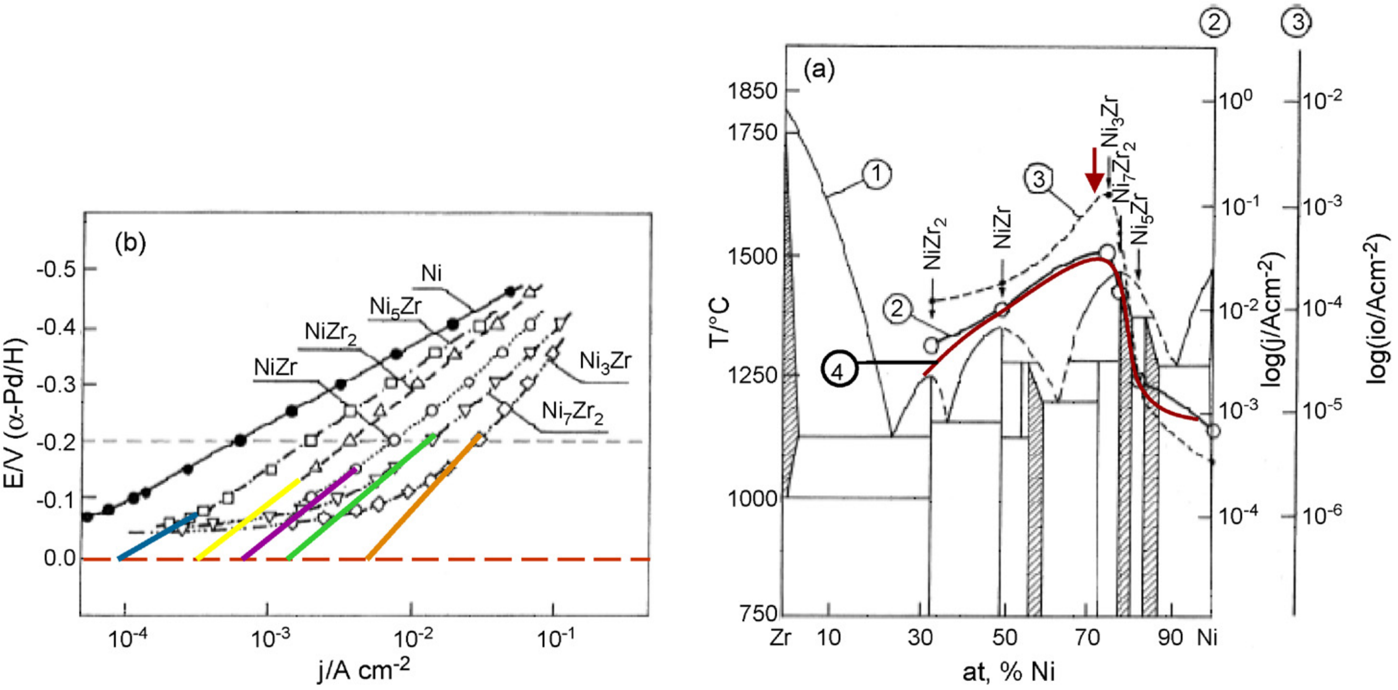

Fig. 1. Electrocatalytic activities of various intermetallic phases (polished below 1.8 in the roughness factor) along Zr–Ni phase diagram (curve 1) for the HER, taken as the exchanged current (j_o, close circles, curve 3) and relative current density changes (j, closed circuits, curve 2) at constant overvoltage (−0.2 V) and plotted together with the cohesive energy of intermetallic phases (curve 4, arbitrary units).