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Novel dynamic effects in electrocatalysis of methanol oxidation on supported nanoporous TiO_2 bimetallic nanocatalysts

Maria Hepel[a,*], Indeewari Dela[a], Tadeusz Hepel[b], Jin Luo[c], C.J. Zhong[c]

[a] *Department of Chemistry, State University of New York at Potsdam, Potsdam, NY 13676, USA*
[b] *Institute of Nanotechnology, Potsdam, NY 13676, USA*
[c] *Department of Chemistry, State University of New York at Binghamton, Binghamton, NY 13902, USA*

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Abstract

New dynamic aspects of the catalysis of methanol oxidation reaction (MOR) have been studied using quantum mechanical calculations applied to the support–catalyst cluster interactions and surface diffusivity of adsorbed intermediates. For very small catalyst–support clusters, we have found a strong enhancement of the ligand effect for bimetallic catalysts of the type Pt_nM_m attributed to the decreased local density of states near the Fermi level of Pt atoms neighboring the additive metal atom M. This enhancement results in a decreased barrier for surface diffusion of adsorbed CO_{ad} through the *cooperative diffusion* mechanism, based on structural relaxation of the catalyst–support cluster, proposed in this work. The strong ligand effect dominates over the Schwoebel potential and trapping well effects, being responsible for accumulation of poisoning intermediates at step sites on the catalyst surface and gradual decrease of catalytic activity with decreasing size of catalyst nanoparticles. The lattice relaxation and strong ligand effects in small catalyst–support clusters lead to lower adsorption energy for CO_{ad} and thus, to higher reactivity and mobility of reactants and intermediates. The experimental investigations included submonolayer films of bi-functional catalysts (PtRu, PtFe) deposited on novel nanostructured supporting materials, designed with the goal of achieving high variability of their electronic and chemical properties to influence the catalytic activity of sub-monolayer catalyst. The mesoscopic TiO_2 supporting film formation was investigated using EQCN, pulse voltammetric and AFM techniques. The conditions for the formation of monodispersed TiO_2 nanoparticles with regular nanopores (nanotubes), 20–80 nm in diameter, were described. It follows from EQCN and voltammetric measurements and AFM image analysis that the nanopores are formed by a dissolution-precipitation mechanism. The catalysts, Pt and PtRu, deposited on supporting nanoporous TiO_{2-x} films, were used to study MOR. A lower poisoning effect for cluster PtRu on a TiO_{2-x} support film than that for unsupported PtRu or bare Pt catalysts has been observed. These effects have been attributed to differences in CO_{ad} binding energy and lowering of activation energy for surface mobility leading to a more facile 2D diffusion of CO_{ad} from Pt sites to Ru and the supporting TiO_{2-x}. The substrate–catalyst interactions were further investigated using quantum mechanical calculations performed for a model TiO_2 nano-ring (representing an orifice of a TiO_{2-x} nanotube studied experimentally) with adlayers of Pt, Ru and Fe catalysts. We have found unusually strong electron delocalization effects for Pt_2Fe_2 clusters on $(TiO_2)_4$ as compared to $(TiO_{2-x})_4Pt_2Ru_2$. We have also analyzed various states in surface diffusion of CO_{ad} on bimetal clusters supported on $(TiO_2)_n$ and observed considerable dynamic widening of metal-to-metal atom distances induced by CO adsorption (up to 9% for Pt–Pt distance and up to 15% for Fe–Fe distance). We propose that this new dynamic effect leading to *cooperative surface diffusion* may be further explored in designing novel nanoparticle catalysts.
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Keywords: Electrocatalysis; Cooperative surface diffusion; Ligand effect; Nanoparticles; Methanol oxidation; Fuel cells; Nanoporous TiO_2

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1. Introduction

The electrochemical oxidation of methanol, studied extensively in conjunction with the development of fuel cells [1–18], is a complex electrocatalytic process proceeding through six electron transfers per molecule and is complicated by slow physisorption of methanol on an electrode surface, generation of poisoning intermediate, CO_{ad} and incomplete oxidation paths with the formation of formaldehyde, formic acid and other species.

The methanol oxidation reaction (MOR) is best catalyzed on bimetallic catalysts such as Pt-Ru [1–4], forming two kinds of sites on a catalyst surface: one with high activity toward dehydrogenation process (e.g. Pt sites) and one providing oxygen species

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[*] Corresponding author. Tel.: +1 315 267 2267; fax: +1 315 268 1709.
E-mail address: hepelmr@potsdam.edu (M. Hepel).

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(e.g. Ru sites), for instance, from weakly bound OH groups or adsorbed water molecules [19]. This bi-functional mechanism [4] operates for alloys, where many nearest neighbor pairs such as the PtRu, can be encountered. It has been found recently [20] that it can also operate in two-phase catalysts, for instance: Ru islands on a Pt surface, where the edge sites Pt|Ru become very active toward MOR catalysis. Profound effects of metal adatoms such as Pb, Sn, Ru, etc., at submonolayer coverages on catalytic activity of a Pt electrode have been investigated [3,20–22]. Studies on single crystal Pt electrodes have shown [8,23,24] that the presence of adsorbing anions may decrease the catalyst activity due to competitive adsorption with methanol.

The greatest challenge in catalyst development for MOR has been the problem of CO_{ad} poisoning [7], although the pathway without CO_{ad} formation has also been investigated [24–27]. At the electrode potentials of interest to fuel cell applications, CO_{ad}, once formed, is not oxidized electrochemically [24,28–35] unless active OH species [19,36–37] or water molecules [6,19,38] present on a nearest neighbor site are available. In general, atoms of less noble metals can form OH species from water more readily than Pt would, and thus, bimetallic components enhance catalytic properties of Pt based catalysts. On the other hand, the rate of CO_{ad} oxidation can be further increased by reducing the adsorption energy of CO_{ad} on Pt sites, which can be brought about by weakening the CO–Pt bond through changes in electronic properties of surface Pt atoms. For instance, on the basis of density functional theory (DFT) calculations performed by Koper et al. [128], lower energy has been predicted for CO_{ad} binding to a Pt adatom on a Ru(0 0 0 1) surface than for a Pt adatom on a bulk Pt. According to Norskov and co-workers [39,40] and Spendelow and Wieckowski [7,41–43], CO binding to Pt atoms adjacent to other metal M (such as Ru) is weakened due to the downshift of the Pt d-band center resulting from charge transfer from Pt to M atom, which reduces flooding of the CO π^* anti-bonding orbital and back-donation from CO σ to Pt. This constitutes the ligand theory, supported by experimental evidence from ^{13}C NMR [41], XPS [42,43], EXAFS [44,45], IRRAS [46,47] and FT-IR [48] measurements. The ligand effect is now well documented [49–60] and its contribution to the catalytic activity evaluated [7]. One inherent problem associated with the ligand effect is the increased barrier for surface diffusion [54,61], which may restrict the adsorbate spillover effects, e.g. for OH_{ad} from Ru islands to Pt substrate [62]. As indicated recently [63], the OH_{ad} spillover should be limited to the neighboring Pt atoms. In different mechanisms of methanol oxidation proposed so far, the surface mobility of adsorbed reactants and intermediate [64,65] is either considered to be insignificant (as in the theory of 2D nucleation and growth of CO_{ad} and OH_{ad} islands [66–69]) or very high and essential (as in the mean field approximation theory [38,54,70–71,86]). The surface diffusion of CO_{ad} on various substrate materials has been studied as a model system [38,54,61,72–80] using such innovative techniques as the electrochemical nuclear magnetic resonance (EC NMR) [72–74], providing unique data on surface mobility and electronic effects. The surface mobility is also taken into account in the theory of the active site concept [18,75,78,81] where the interplay of surface reactivity and adsorbate mobility on different crystal faces, steps and edges are considered. Differences in catalytic activity on terraces and defects (including steps, edges, etc.) have long been recognized [7–10,82–89] but became of primary interest with the emergence of nanotechnology and the discovery of diminishing activity of nanoparticle catalysts with the decreasing particle size below ca. 3 nm, reported by several groups [75,90–96]. Studies of well defined monodisperse size-tunable core–shell nanoparticles [97–111] have shown that different kinds of size effects proliferate in the nanoworld and influence such different properties as light absorption [112], melting point [113], standard electrode potential [114], photoelectric yield [115,116], surface plasmon frequency [117,118], etc. The size effect in catalysis of methanol oxidation on ultrasmall nanoparticles Pt_n (with size: 1–3 nm) has been attributed to the stronger binding of CO_{ad} [76,82,96,119–125] due to large surface strain [126] induced by high curvature of small nanoparticles and the resulting contraction of the lattice parameter, which may be as high as 5% [82]. A considerable change in chemisorption and catalytic properties may then likely result [126] from an upward shift in the d-band center, toward the Fermi level. The higher availability of d-band electrons at Fermi level makes the Pt–CO bond stronger [39,42,127] in $Pt_n|CO_{ad}$. Various aspects of CO bonding to Pt, Ru and other metals have been discussed in the literature [7,128–131]. Markovic’ et al. [132] have shown that distribution of Mo atoms and associated with it ligand effect and catalytic activity can be different on different faces of PtMo nanocrystals.

To further enhance catalytic processes of MOR, the catalyst–support interactions have been investigated on the notion that in a similar mechanism to the metal on metal epitaxy [133], the electronic properties of a catalyst overlayer can be altered. Supporting materials such as the transition metal oxides [134–149], alumina, carbon nanotubes, HOPG and glassy carbon have been considered. Catalytic enhancements of MOR and oxygen reduction reaction using metal catalysts supported on WO_3 have been reported [143–148]. The enhancement of MOR has been attributed to the hydrogen spillover. Note that the slow dehydrogenation occurring during the dissociative adsorption of methanol has been encountered by Ross and co-workers [150] at lower temperatures and for higher Ru content in a Pt-Ru catalyst. The metal cluster size effects for a Au catalyst deposited on a TiO_2(1 1 0) substrate have been investigated in gas phase [91,151] and have shown an increase in Au binding energy with decreasing cluster size down to ca. 2.5 nm. The maximum catalytic activity was found for clusters with diameter of 2.5 nm, which coincides with the metal–semiconductor transition of Au. The latter is a clear evidence of the diminished density of states near the Fermi level for particles smaller than 2.5 nm leading to the decrease in the strength of bond to adsorbates such as CO_{ad}.

In this work, we have explored the effects the supporting materials may have on electronic and interfacial properties of sub-monolayer catalyst films. In this respect, a semiconducting support offers an extraordinary variability in terms of electronic characteristics (high electronic conductance, surface trapped holes, surface states, band bending, etc.), chemical composition (non-stoichiometry, surface acceptor states), modifiable morphology and, at least in the case of TiO_2 being the subject of this

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