Catalysis Today 158 (2010) 29–34

Contents lists available at ScienceDirect

Catalysis Today

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

Electrochemical and density functional studies of the catalytic ethylene oxidation on nanostructured Au electrodes

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ARTICLE INFO

Article history:
Available online 19 June 2010

Keywords:
Electrocatalysis
Ethylene oxidation
DFT
Gold clusters
Nanostructured Au electrodes
Quartz crystal microbalance

ABSTRACT

Electrocatalytic oxidation of ethylene on gold was investigated by means of differential electrochemical mass spectroscopy (DEMS), quartz crystal microbalance (QCM) and DFT calculations. The product analysis indicates a selectivity of the polycrystalline gold towards formation of acetaldehyde. The oxidation process on fresh surface prepared by surface gold oxide reduction, on the other hand, forms mainly carbon dioxide. The oxidation process encompasses metal dissolution. DFT based analysis of the ethylene oxidation on Au clusters was employed to interpret the experimental data. DFT calculations support experimental findings and indicate possible reaction mechanisms of catalytic reactions. DFT calculations point to the different reactivity on individual types of surfaces and different types of clusters.

1. Introduction

The control of the selectivity of the (electro)catalytic processes represents the main challenge in the field of the 21st century. The issue of selectivity is of particular importance in electrode processes involving small organic molecules featuring both single as well as double bonds. In particular oxidative processes connected with oxygen transfer to the molecule like, e.g., oxidation of aliphatic alcohols or insertion of oxygen into double bond [1]. In the latter case there is a need to develop electrocatalytic materials for selective oxygen insertion. One of the possible approaches may be the use gold nanoparticles and clusters which are known to facilitate reactions mechanism unknown on conventional catalysts [2]. In the case of the ethylene oxidation experimental studies indicated the preferential carbon dioxide formation on platinum, the same processes on gold surface yield mixtures of partially oxidized products. In the case of ethylene oxidation on gold the ex situ chromatographic detection found that the oxidation leads to a mixture of aldehydes [3,4]. These studies were later corrected by application of in situ techniques which predicted also formation of CO_2 [5]. As a rule, it is expected that alkenes are oxidized in adsorbed state when both molecules form a flat adsorbate at the electrode via interaction of π electrons of the alkene double bond [5–7].

The fundamental understanding of catalytic reactions at gold nanostructured electrodes is, at present, rather limited. Computational approach to ethylene reactivity providing potential energy curves for different reactant and product conformations may be instrumental in matching the desired mechanism with catalytic surface. The number of theoretical studies (preferably DFT) using cluster approach for modeling the interaction molecules with metal interface has been growing, recently. Calculations have shown the ability to indicate possible pathways for catalytic processes [8–14]. Present work addresses theoretical aspects of the electronic structure of reaction intermediates, ionic distribution at the cluster–solution interface and the more fundamental aspects of looking for transition states in order to map the reaction coordinate of reactions that take place in ethylene oxidation at metal nanoparticles, modeled by Au clusters.

2. Experimental

2.1. Electrochemical experiments

All electrochemical experiments were performed in 0.1 M solution of $HClO_4$ (Flukka, p.a.) in Millipore MilliQ quality de-ionized water. The perchloric acid solutions were saturated with gaseous ethylene (98% Linde) prior to electrochemical experiments. All chemicals were used as received.

The interactions of ethylene with electrode materials were studied by cyclic voltammetry on compact polycrystalline gold disc electrodes with diameter of 4 mm mounted in PTFE holder. The in situ gravimetric experiments were done on a polycrystalline gold forming one of the contacts of a 10 MHz AT-cut quartz crystal (ICMFG OK, USA). The gold substrate was of keyhole shape, sputtered directly on quartz without any under-layer. Piezoac-

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doi:10.1016/j.cattod.2010.05.025

tive area of the crystal was 0.22 cm^2. All electrochemical and EQCM experiments were performed in a one-compartment glass cell using three-electrode arrangement with Pt wire auxiliary and saturated calomel reference electrode. The potential control during the experiments was achieved using PAR 263 A potentiostat. The frequency change of the quartz crystal was monitored using in house built EQCM circuitry designed according to that of Bruckenstein [15]. It needs to be noted that the most relevant gold morphology providing relevant data to complement the DFT results should be nanoparticulate gold. On the other hand, the fact that metal nanoparticles are usually stabilized by surface-active species (which can significantly alter the electrocatalytic activity) makes the use of nanoparticulate gold catalysts less convenient.

The analysis of reaction products was performed using the differential electrochemical mass spectroscopy (DEMS). All DEMS experiments were performed on polycrystalline gold sputtered directly on a PTFE membrane (WL Gore) placed in a home-made Kel-F single compartment cell and three electrode arrangement described in [16]. The DEMS apparatus consisted of Prisma^{TM} QMS200 quadrupole mass spectrometer (Balzers) connected to TSU071E turbomolecular drag pumping station (Balzers).

2.2. Computational details

Ground state DFT calculations were performed in Gaussian 03 [17]. Gold clusters were optimized without any geometrical constraint. The calculations were performed for clusters of different structure and size in order to get realistic models of real clusters approximately composing of 100–200 atoms. Optimized ground state geometry of clusters was calculated for the several possible spin multiplicities. Stationary states were characterized by vibrational analysis performed at optimized geometries.

In the present investigation, reaction pathways were investigated by means of hybrid density functional theory with the B3LYP functional [18–20]. The open-shell electronic systems were characterized by unrestricted DFT. The energy profiles of ethylene oxidation presented in this work were obtained using geometrical fixed cluster Au$_{22}$. Within G03 calculations the quasirelativistic effective core pseudopotentials LANL2DZ (Los Alamos ECP) [21] and the corresponding optimized set of basis functions for Au were used. For H, C and O atoms, 6-31G* [22–23] polarized double ζ basis set was used.

The conductor-like screening model (COSMO) [24] was used for modeling of the solvent influence. External electric field was applied using electric dipole field 0.065 a.u. which modeled the electrochemical potential around 1 V.

3. Results and discussion

3.1. Ethylene oxidation on gold – DEMS approach

Typical cyclic voltammograms of the ethylene oxidation on polycrystalline gold recorded at 5 mV/s is shown in Fig. 1. Ethylene is oxidized in both scans in the potential window between 0.6 V and 1.2 V (vs. SCE). The upper limit of the potential window coincides with the onset of the surface gold oxide formation.

The oxidation of ethylene on Au can be followed by differential electrochemical mass spectroscopy (DEMS). While the DEMS data suggest CO$_2$ as the only reaction product for the ethylene oxidation on platinum the oxidation on gold proceeds via more complex pathway. The fragments of the consumed ethylene (e.g. $m/z = 27$) decrease in the same potential region where an increase of the anodic current is recorded. The ethylene related signals show gradual recovery at potentials positive to 1.0 V; they do not reach, however, the original values and show further slow decrease at potentials positive to 1.5 V, i.e. in the region where parallel oxygen evolution is observed. The ethylene signal shows very little variance with potential as long as the surface of the electrode is oxide covered. The anodic process following the reduction of surface oxides may be again assigned to ethylene oxidation (see Fig. 2). The signal of ethylene consumption is inversely tracked by signals attributable to fragments of ethylene oxidation products characterized by m/z values of 15, 29, 44 and 43. A fragment with m/z of 32, attributable to molecular oxygen, can be also detected at potentials positive to 1.4 V.

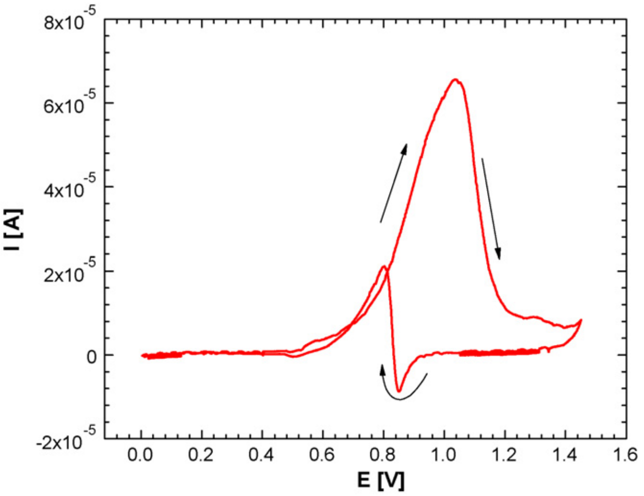

Fig. 1. Cyclic voltammogram of a polycrystalline gold electrode in 0.1 M HClO$_4$ saturated with ethylene at 5 mV/s.

It ought to be noted that the small ethylene concentration decrease at potentials positive to 1.3 V is not inversely tracked by the product mass fragment with m/z of 15, 29 or 43. The only signal which reflects the ethylene consumption in this potential region is the mass fragment with m/z of 44 attributable to formation of carbon dioxide.

The fragments of reaction products are characteristic for either acetaldehyde or oxirane. The formation of the oxirane can be practically ruled out due to weak signal of fragment with the m/z of 15. Relatively strong signal of the fragment with m/z of 44 indicates that the acetaldehyde formation is accompanied with simultaneous carbon dioxide evolution. The selectivity of the polycrystalline gold towards different reaction products seems to be affected (besides of the electrode potential) also by history of the electrode surface. While the fragments attributable to acetaldehyde formation (m/z of 15 and 29) dominate in the potential region between 0.6 V and 1.0 V in the anodic scan, the ethylene consumption in the same potential interval of the cathodic scan (i.e. on the re-activated surface after surface oxide reduction) seems to be accompanied mainly by CO$_2$ formation. Despite this difference in gold surface selectivity the observed results in principle agree with those reported previously [5].

Since the oxidation of the alkenes on polycrystalline gold may in principle affect the electrode mass, one can use the electrochemical quartz crystal microbalance (EQCM) technique to gather additional information about the studied processes. Although the experimental implementation of EQCM to study the ethylene oxidation is rather straightforward, the analysis of the measured data is complicated by the fact that the anodic polarization of the gold electrode in pure supporting electrolyte solution (0.1 M perchloric acid), i.e. in the absence of dissolved ethylene, is not electrode mass neutral.