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Counting surface redox sites in carbon-supported electrocatalysts by cathodic stripping of O deposited from N_2O

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ABSTRACT

Methods of determining *in situ* the electrochemically active surface area of bulk noble metal electrodes (e.g., underpotential deposition of a strongly interacting sorbent followed by columbic stripping) may not be appropriate for certain base metals supported on electroactive supports, such as carbon, because of the difficulty of finding a metal-specific titrant and because the support itself can contribute a very large background current. For example, the coulometric stripping of metal-selective sorbates, like carbon monoxide, works for the *in situ* characterization of certain electrode-supported metals (e.g. Pt, Pd) if applied carefully, but not for base metals, like Cu that do not strongly adsorb the titrant. Moreover, in scoping studies, we found that underpotential deposition of Tl on carbon-supported Cu failed to be selective for the copper. Here we present the use of gentle oxidation of the metal domains using N_2O as the oxidant, followed by cathodic stripping of the surface oxide. The method compares approximately with XRD line broadening for characterizing ~10 nm particles of Cu supported on graphite felt. More significantly, we show that the method usefully normalizes the rates of two electrochemical hydrogenation reactions: conversion of nitrobenzene to aniline and conversion of benzaldehyde to benzyl alcohol.

1. Introduction

Measurement of site-normalized activities (turnover rates) of supported electrocatalysts shows that the normalized electrocatalyzed rates can vary significantly with the size, shape, composition and spacing between the particles. While most of the information comes from the electrochemical reduction of dioxygen catalyzed by Pt (Table 1), it is plausible that similar effects may be found for other reactions and other catalysts.

Those physical characteristics of the supported particles can be measured using *ex situ* techniques, e.g., X-ray diffraction or electron microscopy. However, chemical and morphological changes upon removing the catalyst samples from the electrochemical cell can interfere with determining the sizes of the metal particles in use. For catalysts derived from platinum group metals, *in situ* estimation of the electrochemically active sites can be determined by underpotential deposition (UPD) of hydrogen [5] or cathodic stripping of adsorbed carbon monoxide [6]. However, for electrocatalysts containing base metals (viz. transition metals, like Cu), sorption methods can be confounded by reactions occurring on the support (e.g., activated carbon) or a too vigorous reaction of the metal particle with the adsorbate. For example, the underpotential deposition of Tl, serves to count the electrochemically active surface area of Cu foils and wires [7] but, when we applied it to catalysts consisting of carbon-supported copper, we, like others [8,9], observed a very large background current that overwhelmed the deposition current associated with the supported metal particles. Likewise, while the use of oxygen dissolved in solution can be used to count the electrochemically active surface of Au, where only a surface oxide forms [10], base metals can form multilayers of the oxide which complicates enumerating just the surface sites.

Here, we present the use of a gentle oxidation, using N_2O, followed by coulometric reduction to count redox sites on the metal particles of base metals supported on an electroactive support. The use of N_2O to measure the fractional exposure of catalysts containing base metals was introduced by Osinga et al. [11] to quantify the rates of reactions catalyzed by supported and bulk Cu. Its extension

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Table 1
Characteristics affecting activity of supported Pt electrocatalysts for oxygen reduction.

Characteristic	Observed effect on turnover rate	Range studied
Metal particle size [1,2], d_p	~20-fold increase with d_p	$1\text{ nm} < d_p <$ bulk metal
Interparticle distance [3], Δ	~3-fold decrease with Δ	$1\text{ nm} < \Delta < 40\text{ nm}$
Metal particle composition [4]	~2-fold change	Pt, PtFe, PtNi, PtCo, PtCu
Catalyst support [4] (but, convoluted with d_p)	~1.5-fold change	$0.16 < I_{110}/I_{111} < 0.22$

to characterizing electrocatalysts provides a selective way to count redox sites on the surfaces of those catalysts, notably for samples containing very small domains that may be missed by x-ray diffraction or electron microscopy. As a first test of the titration, we have applied the method to normalize the reaction rates measured for Cu/C-felt catalysts that have been used for the electrochemical reduction of nitroaryl substrates and electrochemical reduction of benzaldehyde. The electrochemical rates were measured over ranges of applied potential to test whether the number of titrated sites appeared to remain constant across conditions that could irreversibly restructure the redox domains [12].

2. Experimental

2.1. Catalyst preparation

The catalysts consisted of Cu supported on graphitic carbon, prepared by incipient wetness impregnation using water solutions of copper(II)acetate monohydrate (Sigma-Aldrich) onto commercial graphitic felts (0.6 cm thick, Alfa-Aesar #43200). The felts had been rendered hydrophilic either by mild oxidation at 400 °C in dilute, flowing oxygen (1, 2 and 4 wt% samples) or by immersion in concentrated nitric acid at 80 °C (0.5 wt% sample). In passing, we note that we found that felt oxidized using nitric acid lost its wettability once it had been dried; the mildly oxidized felt retained its hydrophilicity after drying. Typical wet points of the mildly oxidized felt were 11 mL/g. The impregnated felts were calcined in static air to decompose the precursors using a temperature program that ramped from room temperature to 423 K at 2 K/min and then to 673 K at 4 K/min. The samples were maintained at the final temperature for 120 min before cooling (ballistically) to room temperature. Typically, the furnace was loaded with ~ 3 g pieces of the felt-supported samples. We targeted, and achieved, metal loadings in the range of 0.3–4 wt% as determined by ICP (Galbraith Labs).

2.2. Powder XRD

Aliquots of the metal-loaded felts were crushed in a mortar and pestle then spread on the sample stage. The diffraction patterns were collected on a Rigaku Mini Flex II bench top X-ray diffractometer. The samples were scanned at a rate of 0.1°/min from $2\theta = 15$ to 80° using the Cu-Ka radiation (0.154056 nm, 30 kV and 15 mA). The sizes of the crystalline domains were estimated using the Scherrer formula. Instrumental line broadening was determined with the NIST standard, LaB_6.

2.3. N_2O-titration

The sample pretreatments and titrations were performed in a jacketed electrochemical H-cell (Adams & Chittenden Scientific Glass) using cellulosic filter paper (Whatman, 1001-185) as a membrane to separate the anode and cathode chamber. We also tested the use of a Nafion® membrane, which worked but we preferred to use the filter paper because it performed more consistently and decreased the overall cell resistance. The electrolyte was a solution of 20 mM ammonium hexaflurorophosphate (NH_4PF_6, Aldrich, ≥95%) in deionized H_2O (18.2 MΩ cm). A 12.7 cm length of Pt wire (0.58 mm in diameter) was used as the anode. The test sample served as the cathode and was connected to the potentiostat (CH Instrument Electrochemical Analyzer Model 1100A Series), and completely submerged in 60 mL of the electrolyte. An Ag/AgCl reference electrode (Harvard Apparatus 6237653) was positioned next to the cathodic electrode. Currents were measured at a sensitivity of $4 \cdot 10^{-4}$ A/V with scan rates of 0.01 mV/s. The titration consisted of these five steps:

(1) pretreatment to reduce the metal sites
(2) measurement of the background current
(3) oxidation of the metal sites using N_2O
(4) electrochemical reduction of the adsorbed O
(5) repeated measurement of the background current to verify completion of the reduction.

First, N_2 was bubbled through the electrolyte to deoxygenate it and then the cell was sealed. Except as noted below, the anolyte and catholyte were stirred using magnetic star bars spinning at 250 rpm. In Step 1, a half-cell potential of −2.0 V was applied to the cathode for 15 min to ensure reduction of sample. During the reduction, the surface of both anodic and cathodic electrodes became covered with bubbles, O_2 on the anode and H_2 or N_2 on the cathode. A gentle tap served to remove the gases from the surface of the electrodes and rewet them with the electrolyte. After the reduction step, the magnetic agitation was stopped and an IR compensation measurement was performed. The resistance ranged between 10 and 15 Ω. When we used a Nafion® membrane, the cell resistance ranged inconsistently between 100 and 900 Ω. Next, in Step 2, the background (blank) current was measured at half-cell potentials ranging from −0.2 to −2.0 V. Again, gentle taps served to remove the gas bubbles from both electrodes. In Step 3, a 1 mL solution of de-ionized water saturated overnight with N_2O gas (Aldrich, 99%) was added to the cathode compartment, which was stirred for 10 min at 250 rpm to gently oxidize the surface of the metal. No potential was applied to the system during the N_2O dosing. Excess (unreacted) N_2O was removed from the electrolyte by again purging it with N_2 gas with stirring for 15 min. Then, the flow of N_2 and the magnetic stirring were stopped, and the bubbles generated during the oxidation process were removed with a gentle tap. We note that the membrane should have served to prevent oxygen generated in the anode compartment from crossing into the cathode compartment. The experiments described below that used wires instead of carbon-supported metals support that notion.

The current that flowed during reduction of the oxidized electrode ($I_r(t)$, Step 4) was scanned at half-cell potentials from −0.2 to −2.0 V. The second background measurement ($I_b(t)$, Step 5) was measured at half-cell potentials ranging from −0.2 to −2.0 V to ensure complete electrode reduction. The current associated with the titration ($I_a(t)$ was calculated as the difference $I_r(t) - I_b(t)$, and then integrated to estimate the charge, *C*, associated with the reduction of the titrated surface oxide