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*J. Phys. Chem.*, **1987**, 91 (19), 5083-5087 • DOI: 10.1021/j100303a040

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Electrochemical Investigation of the Electron-Transfer Kinetics and Energetics of Illuminated Tungsten Oxide Colloids

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Electrochemical charge collection techniques were used to study the effects of platinization and reduction on the electron-transfer (et) kinetics and energetics of illuminated tungsten oxide colloids. From the mediated charge collection experiments, the quasi-Fermi level for electrons, \( nE_F^* \), was found to be +0.33 V vs. NHE (pH 0) for WO\(_3\) and shifted to +0.21 V for the reduced (H\(_2\)WO\(_4\)) and platinized (Pt(WO\(_4\))) tungsten oxides. The platinization of WO\(_3\) also caused it to be irreversibly reduced. Silica particles coated with a monolayer of WO\(_3\) displayed an \( nE_F^* \) which was 170 mV negative of that for WO\(_3\). The photocurrent transients for direct et to a collector electrode were potential dependent and were used to measure \( k^2 \), the standard heterogeneous rate constant for et, by using a previous treatment derived for iron oxides. The reduction of WO\(_3\) decreased \( k^2 \), while platinization slightly increased it.

Introduction

We report here an investigation of the kinetics of direct electron transfer (et) from a WO\(_3\) particle to an electrode in solution, using charge collection techniques.\(^1\) Previously, a model for direct et was developed with iron oxide particles.\(^2\) Here, we apply those concepts to WO\(_3\) to study the effect of platinization and tungsten bronze formation on the et kinetics and compare the properties of WO\(_3\) to those of the iron oxides.\(^2\) Values for \( nE_F^* \), the quasi-Fermi level for electrons under illumination, were measured by mediated charge collection techniques.\(^1\) This level in particles is analogous to the flat-band potential for n-type semiconductor electrodes and is a measure of the reducing power of photogenerated electrons in semiconductor colloids and particles. A silica particle coated with a monolayer of WO\(_3\) was prepared for study. This material should mimic a small particle semiconductor colloid with less bulk electron/hole (e\(^-\)/h\(^+\)) recombination.

As light-collection systems, semiconductor colloids offer some desirable properties.\(^3\) Their small particle diameter affords a high surface area, which is needed for efficient electron and hole transfer to solution and surface species. The heterogeneous rate constants that characterize such reactions for semiconductors are often lower than those for noble metals,\(^4\) thus necessitating a large surface area to increase the overall rate. Their small diameter allows both charge carriers generated in the bulk to diffuse to the surface before recombination.\(^5\) This type of behavior makes each particle operate like a miniature photoelectrochemical cell.\(^6\)

The photoelectrochemistry of single-crystal and polycrystalline WO\(_3\) electrodes has been studied extensively,\(^7\) and WO\(_3\) has also been investigated as an electrochromic material.\(^5\) Kransnovskii


TABLE I: Energetic and Kinetic Data for Different Forms of Tungsten Oxide

<table>
<thead>
<tr>
<th>Substance</th>
<th>$n_{f7,\gamma}$</th>
<th>$d$, nm</th>
<th>BG, eV</th>
<th>BE, eV</th>
<th>$X$</th>
<th>$N_{p}$, cm$^{-2}$</th>
<th>$k_{p}$, cm/s</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO$_3$</td>
<td>0.33 ± 0.01</td>
<td>0.32</td>
<td>2.7</td>
<td>35.0</td>
<td>0.00005</td>
<td>5.0 x 10$^{11}$</td>
<td>1.0 x 10$^{-4}$</td>
<td>0.83</td>
</tr>
<tr>
<td>H$_2$WO$_4$</td>
<td>0.21 ± 0.04</td>
<td>0.42</td>
<td>1.47</td>
<td>35.3</td>
<td>0.032</td>
<td>3.2 x 10$^{10}$</td>
<td>5.6 x 10$^{-4}$</td>
<td>0.75</td>
</tr>
<tr>
<td>Pt/WO$_3$</td>
<td>0.21 ± 0.02</td>
<td>0.54</td>
<td>1.48</td>
<td>35.5</td>
<td>0.008</td>
<td>8.0 x 10$^{19}$</td>
<td>2.5 x 10$^{-6}$</td>
<td>0.86</td>
</tr>
<tr>
<td>SiO$_2$/WO$_3$</td>
<td>0.16 ± 0.01</td>
<td>0.18</td>
<td>3.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>single-crystal WO$_3$</td>
<td>0.74</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>thermally oxidized 0.24$^d$ WO$_3$</td>
<td>0.24$^d$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$n_{f7,\gamma}$ quas-Fermi level for electrons measured vs. NHE at pH 0.0; $d$, hydrodynamic diameter; BG, band gap by photoacoustic method; BE, binding energy of the W 4f$7/2$ state; $X$, mole fraction of W$^4+$ in tungsten oxide; $N_{p}$, corresponding doping density; $k_{p}$, standard heterogeneous rate constant; $\alpha$, transfer coefficient. $^a$Error limits are the least-squares standard deviation. $^b$Taken from ref 4h. $^c$Taken from ref 4j.

et al. described the oxidation of water by mediated particulate WO$_3$ in the presence of ferric ions. Darwent and Mills further developed this work by studying how oxygen evolution was influenced by deposition of RuO$_2$, Pt, Rh, or Ru on WO$_3$. Grätzel et al. demonstrated that irradiation of WO$_3$ dispersions with Ag$^+$ ions as electron acceptors produces oxygen more efficiently and Cl$_2$ can be generated by oxidation of Cl$^-$.

Pulse radiolysis techniques to measure the flat-band potential of WO$_3$ colloids have also been reported.

Experimental Section

The tungsten oxides used in this study were tungsten trioxide (WO$_3$), tungsten bronze (H$_2$WO$_4$), platinized tungsten oxide (Pt/WO$_3$), and tungsten oxide deposited on silica (SiO$_2$/WO$_3$). WO$_3$ powder was used as obtained from Alfa Products (Danvers, MA) (99.9%). H$_2$WO$_4$ was prepared by passing H$_2$ over WO$_3$ at 375 °C for 3 h. The $x$ value was determined by the procedure of Choin and Marion by dissolving the H$_2$WO$_4$ in boiling, saturated K$_2$CO$_3$ solution followed by the addition of AgSCN. Ag metal was formed by reaction with the reduced tungsten (formally W$^0$). The Ag metal is filtered, washed, and dissolved in HNO$_3$ and the amount of Ag$^+$ determined by a Volhard titration.

From the amount of Ag$^+$ produced, the extent of reduction, $x$, is calculated. Pt/WO$_3$ was prepared in a modification of the procedure of Grätzel. WO$_3$ (0.22 g) was suspended in 100 mL of deionized water containing 0.4 mL of 0.1 M H$_2$PtCl$_6$ solution. After 16 h of irradiation with a Xe lamp, 40 mL of formaldehyde was added, and the material was photolyzed for another 1.5 h. The material, which had turned blue-grey, was washed and centrifuged 5 times and vacuum dried. After photolysis, the material was heated in oxygen at 500 °C for several hours and then cooled under an oxygen atmosphere.

The extent of photolysis was determined gravimetrically by dissolving the WO$_3$ in boiling, saturated K$_2$CO$_3$ solution, filtering the Pt, washing it with H$_2$O and HNO$_3$, and drying. The extent of photolysis was 2.5 wt% for WO$_3$. SiO$_2$/WO$_3$ was prepared by a controlled hydrolysis technique. A WCl$_6$ solution in dry CH$_2$Cl$_2$ (prepared in a glove box) was allowed to hydrolyze on SiO$_2$ (Degussa powder; dried at 140 °C for 4 h) in dry toluene under high-purity N$_2$. This mixture was stirred and refluxed for 24 h. The mixture was then filtered in air, washed with toluene, acetone, and methanol, and dried. During filtration and washing, the material changed color from a dark blue to white, which represented hydrolysis of the residual W–Cl bonds. The hydrodynamic diameter of the SiO$_2$ was measured before and after the treatment and was found to be unchanged.

The X-ray powder pattern showed no peaks for WO$_3$. Suspending these materials were prepared by sonication the dried powders in deionized water. The concentrations were 1 mg/mL.

The hydrodynamic diameters of the colloids were measured by photon correlation spectroscopy with the equipment described previously and are listed in Table I.

In binding energy of the tungsten 4f$7/2$ state was measured by X-ray photoelectron spectroscopy (Vacuum Generators ESCA LAB II) using Mg K$_\alpha$ radiation. To compensate for charging effects, WO$_3$ was assigned a value of 35.0 eV. The Pt 4f$7/2$ state was observed on Pt/WO$_3$ at 70.9 eV. The photoacoustic measurements were performed with the same equipment as previously described.

The solutions were placed in an electrochemical cell that was equipped with an optically flat Pyrex window for uniform illumination. The cell was irradiated with a 2.5-kW ozone-free Xe lamp. Immersed in the colloidal solution was a platinum flag electrode whose potential was held constant vs. a saturated calomel electrode (SCE) by a Princeton Applied Research (PAR) Model 173 potentiostat (Princeton, NJ). The Pt counter electrode was isolated by means of a glass frit. Before any measurements were made, the solution was deaerated with N$_2$. The solutions were uniformly illuminated and stirred well. The current–time curves were recorded on a Soltect XY recorder (Sunnyvale, CA).

In studies of direct electron transfer from particle to electrode, the photocurrent–time transients were recorded at different electrode potentials in the presence of scavenger but without a mediator present. A voltammogram was constructed by plotting the steady-state photocurrent vs. electrode potential. Ru(NH$_3$)$_6$Cl$_3$ was then added and the steady-state photocurrent measured at different pH's. In this case, the electrode potential was held constant at 150 mV positive of the anodic peak potential ($E_{pa}$) for Ru(NH$_3$)$_6$Cl$_3$ in Ru(NH$_3$)$_6$Cl$_3$. The photocurrent observed is the reoxidation of the mediator which was reduced at the particle surface. Photocurrents from direct electron transfer are negligible at this potential. In the absence of tungsten oxide, no photocurrent was observed.

The generation rate of electron–hole pairs, $G$, was determined by using an EG&G (Salem, MA) Model 550 radiometer/photometer and an Oriel 7240 grating monochromator to measure the photon flux. The $G$ value was calculated to be ca. 10$^{19}$ e$^-$/cm$^2$/s, using the known absorption coefficients of WO$_3$ and assuming a quantum efficiency of 1.

Results and Discussion

Electron Mediation. Irradiation of tungsten oxide particles in the presence of an irreversible hole scavenger gives rise to an

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Electron Transfer in Tungsten Oxide Colloids

The potential dependence of the photocurrent for this direct electron-transfer process can be used to measure the standard heterogeneous rate constant $k^2$ as described in the next section. Addition of Ru(NH$_3$)$_3$Cl$_2$ to mediate electron transfer from particle to collector electrode causes a large enhancement in the photocurrent, because electron transfer (et) to the mediator is kinetically fast compared to direct electron transfer to an electrode. Moreover, the total surface area of the particles in contact with solution mediator is many times larger than that contacting the electrode. Following our previous treatment with iron oxide particles, a plot of log $[\text{imid}/(\text{imid}^* - \text{imid})]$ vs. pH should provide a measure of $nE_F^*$, the quasi-Fermi level for electrons under illumination, at any pH, when the reaction at the surface is thermodynamically controlled and where $\text{imid}$ is the steady-state photocurrent that would result if all of the mediator were reduced at the particle surface. At equilibrium under illumination, at any pH, when the reaction at the surface is controlled to the mediator,

$$E^{\circ - nE_F^*} = 0.0591 \log \left( C_R^{n*}/C_O^{n*} \right)$$

where $E^{\circ}$ is pH independent and $E_F^*$ shifts 59 mV per unit of pH (which is common for oxide semiconductors) then a plot of log ($C_R^{n*}/C_O^{n*}$) vs. pH will be linear with a unit slope and an intercept on the pH axis where $E^{\circ} = nE_F^*$. Once the ratio $C_R^{n*}/C_O^{n*}$ is determined, then $nE_F^*$ at any pH will be known. The bulk concentration of reduced mediator at any time can be related to the photocurrent by the expression for mass-transfer-controlled reaction:

$$E^{\circ} - nE_F^* = 0.0591 \log \left( C_R^{n*}/C_O^{n*} \right)$$

where $m$ is the mass-transfer coefficient, $A$ is the area of the electrode, and $F$ is Faraday’s constant. $C_O$ is evaluated from

$$C_O = C^* - C_R$$

and

$$C^* = C_{\text{med}}/FA$$

so that

$$[\text{imid}/(\text{imid}^* - \text{imid})] = C_R/C_O$$

Under the conditions when the et and mass-transfer kinetics at the semiconductor particle surface are so fast that the ratio $C_R/C_O$ represents the equilibrium ratio, a plot of log $[\text{imid}/(\text{imid}^* - \text{imid})]$ vs. $pH$ can be used to determine $nE_F^*$. Typical plots with different forms of tungsten oxide are shown in Figure 1. The $nE_F^*$ values at pH 0 are listed in Table I. The slopes are near the expected 1.0 for a thermodynamically controlled et to mediator as opposed to that previously observed for the iron oxide particles, which showed marked deviations in the slope, indicating a kinetically controlled et to the mediator.

Note that reduction of WO$_3$ to the tungsten bronze, H$_2$WO$_3$, causes $nE_F^*$ to shift slightly to more negative potentials, as does platinization of WO$_3$. Both formation of the bronze and platinization thus appear to cause some reduction of WO$_3$. To examine the extent of this reduction, two approaches were tried. The first was to measure the shift in the binding energy for the W 4f$_{7/2}$ state by XPS (X-ray photoelectron spectroscopy). These values, listed in Table I, show a negligible shift in binding energy. The second technique, which is much more sensitive, is the one of Choain and Marion’ described in the Experimental Section. This method consists of measuring the amount of $W^v$ in the sample. These values are listed in Table I as the mole fraction of $W^v$ in the lattice $X$ and in terms of the corresponding doping density $N_D$, assuming the doping is caused by $W^v$. The $n$-type semiconducting behavior of WO$_3$ is attributed to oxygen vacancies in the lattice.

These oxygen vacancies are compensated by formation of $W^v$ centers. Consequently, the amount of $W^v$ in the lattice provides a reasonably good measure of the doping density, if no other impurities are present. This measurement suggests that the platinization of WO$_3$ results in a more reduced material (see Table I). Furthermore, the reduction process appears to be irreversible. Attempts to reoxidize by heating in an oxygen atmosphere gave no change in the extent of reduction. Since the level of reduction (or doping) is too low to cause a change in the crystalline phase, the probable reason for the irreversible reduction is slow kinetics for reoxidation due to the presence of the platinum. The X-ray powder pattern for WO$_3$ was unchanged by the platinization. Platinization also seems to catalyze the reduction of WO$_3$. For example, irradiating a WO$_3$ suspension for 18 h gives a material with an x of 0.0002, whereas under the same conditions except by adding H$_2$PtCl$_6$ (0.4 mM) x is 0.008. H$_2$O$_{0.008}$WO$_3$ can be reoxidized, and Pt/H$_2$O$_{0.008}$WO$_3$ cannot.

The photoacoustic spectrum of these materials also lends evidence about their reduced state, as shown in Figure 2. The broad band for both Pt/WO$_3$ and H$_2$WO$_3$ extending from about 500 nm into the IR region is a characteristic of reduced tungsten oxides. That $nE_F^*$ is shifted in a negative direction by reduction has been previously demonstrated. From pulse radiolysis studies, Nenadović et al. showed that the accumulation of electrons in the conduction band shifts the flat-band potential in a negative direction. The shift is attributed to a buildup of positive charge from the electrons.

The $nE_F^*$ measured for colloidal WO$_3$ is analogous to the flat-band potential $V_{FB}$ of solid electrodes. The flat-band potentials for single-crystal and thermally oxidized WO$_3$ are also given in Table I. Our value of $nE_F^*$ compares well with the $V_{FB}$ for the thermally oxidized WO$_3$ but differs significantly with the single-crystal value. However, the $V_{FB}$ and band gap (E$_g$) for WO$_3$ appear to depend on the nature of the material and method of preparation, as noted by Di Quarto et al. For example, reported single-crystal $E_g$ values range between 2.2 and 2.8 eV. This variation is probably related to differences in the nature of the material. There are several possible crystal structures for WO$_3$, with the monoclinic form being the most stable at room temperature and many stable phases containing lower valent tungsten (e.g., distorted perovskite type). The degree of crystallinity seems to be important in the physical properties, especially the measured band gap.

Figure 1. Plots of log $[\text{imid}/(\text{imid}^* - \text{imid})]$ vs. pH to determine $nE_F^*$ using Ru(NH$_3$)$_3$Cl$_2$ as mediator.

Figure 2. The broad band for both Pt/WO$_3$ and H$_2$WO$_3$ extending from about 500 nm into the IR region is a characteristic of reduced tungsten oxides. That $nE_F^*$ is shifted in a negative direction by reduction has been previously demonstrated.
electrolyte used to prepare anodized WO₃ affected the dielectric constant. The \( nE^*_F \) for SiO₂/WO₃ is 170 mV negative of that of WO₃. This shift can perhaps be ascribed to the difference in electronic properties of WO₃ as its dimensions become very small and its properties become less like the bulk material and more like those of small clusters. Such effects have been found with semiconductor particles, whose band gap changes as the particle dimensions become very small.\(^{16-18}\) This localization of the energy levels in small particles would also cause the conduction band edge to be situated at higher energies or more negative potentials. Further evidence for this is seen in the photoacoustic spectrum of SiO₂/WO₃ as compared to WO₃ (Figure 2). The measured band gaps, listed in Table 1, are WO₃ (2.7 eV) vs. SiO₂/WO₃ (3.0 eV).

The actual nature of WO₃ on the SiO₂ particles is not clear. Although the amount of WO₃ corresponds to about a monolayer, the WO₃ may also be in the form of small particles on the SiO₂ surface. The expected optical properties for a film thin in only one dimension and particles small in three dimensions are different. SiO₂/WO₃ is unstable in solution and slowly changes color from white to yellow after about 1 h. The dried material after immersion shows no peak in the X-ray powder pattern. If the X-ray pattern shows peaks corresponding to WO₃, Pt/WO₃, and (e) Pt/WO₃.

Figure 2. Photoacoustic spectrum of (a) WO₃, (b) SiO₂/WO₃, (c) SiO₂/WO₃·2H₂O, (d) H₂WO₄, and (e) Pt/WO₃.

...an electrode.\(^{2}\) For the tungsten oxide systems employed here, the photocurrent transients at the various applied potentials. This behavior was found for WO₃, Pt/WO₃, and H₂WO₃. When the electrode potential becomes very positive, the \( i_m \) approaches a limiting value. The shape of the transients depends upon the potential and shows a "spike" at more positive values. A plot of log \( i_m \) vs. electrode potential is shown in Figure 4 for WO₃, Pt/WO₃, and H₂WO₃. The linearity of these plots suggests that the tungsten oxides all follow Tafel-like behavior, analogous to the behavior found for the iron oxides.\(^{2}\)

The change of shape of the transients with potential and the spiked appearance in the presence of a sacrificial reductant was not seen previously with the iron oxides\(^{2}\) or with TiO₂,\(^{1}\) although we recently saw the same behavior with TiO₂ particle dispersions at very positive potentials in the presence of tartrate. No combination of kinetic parameters in the kinetic model would simulate this behavior; neither would inclusion of electron transfer (partial cathodic currents) to oxidized intermediates produce this shape. Photocurrent transients in the absence of a hole scavenger show...
the structure of active sites. For many catalytic reactions, step along a Step Line of Ni(755) dependent. In the potential region where normal behavior is seen, mass-transfer limiting conditions (Figure 4). However, the voltammogram flattens and has the appearance of being under the current-voltage characteristics follow the Tafel relationship.20

Figure 5. Photocurrent transient without hole scavenger for WO3/0.01 M HNO3 and 0.1 M KNO3 at an electrode potential of 0.6 V vs. SCE.

The same spiked shape at positive potentials, in addition to a cathodic components (Figure 5). The cathodic component is the result of et to hydroxyl radicals (or other water oxidation intermediates).19 The fact that this cathodic spike has a small time constant suggests that the cathodic transient component is probably not responsible for the shape of the potential-dependent anodic transient. A more likely explanation is the formation of a blocking layer of particles at the surface of the electrode under illumination. In the presence of a reductant the particles build up a negative charge under illumination because of the accumulation of electrons (as holes are scavenged).16,19 When the potential of the electrode is held sufficiently positive with respect to the point of zero charge, a layer of particles adhering to the electrode surface will form as a result of the Coulombic attraction. This layer blocks charged particles from the bulk solution from reaching the electrode surface and transferring electrons. The steady-state photocurrent then results solely from the collection of electrons from the particles on the surface of the electrode. Evidence for formation of such a layer on the electrode surface is provided by the following experiment. If the electrode is taken out of the colloidal solution after irradiation at a positive potential and placed in a clear solution containing only electrolyte and hole scavenger, a photocurrent is observed that is similar in shape to the photocurrent transients obtained at low overpotentials. The magnitude of the steady-state photocurrent is comparable to the current obtained in the presence of semiconductor particles.

When the particles begin to adhere to the electrode surface, the voltammogram flattens and has the appearance of being under mass-transfer limiting conditions (Figure 4). However, the steady-state photocurrent in this region is still stirring rate independent. In the potential region where normal behavior is seen, the current-voltage characteristics follow the Tafel relationship.20


The transients in this region can be fit by numerical solutions to kinetic expressions that describe the concentration of electrons and holes as a function of time.2 Through this fit, the steady-state concentration of electrons \( N_{e0} \), can be calculated and is used as the concentration term in the Tafel equation:

\[
\log j_{\text{th}} = \log (nFNC_{e0}s + k^0) + (1 - \alpha)nFV/2.303 \tag{6}
\]

where \( j_{\text{th}} \) is the steady-state photocurrent density, \( n \) is the number of electrons, \( k^0 \) is the standard heterogeneous rate constant, \( \alpha \) is the transfer coefficient, \( F \) is \( F/R \), and \( V \) is the overpotential (defined as the difference between the electrode potential and \( nFE_F^* \)). Through the Tafel relationship, the \( k^0 \) values were determined, which allow comparison of the et kinetics from a semiconductor particle to an electrode. Plots are shown in Figure 4, and the \( k^0 \) values are given in Table I. The differences in \( k^0 \) show that the heterogeneous et kinetics are affected by the treatments on the \( \text{WO}_3 \). As in the case of iron oxides,2 the particle size is not as important a variable as the surface and bulk properties in this study, since \( k^0 \) varies by a factor of >200, while the particle size changes by a factor of <2. The et kinetics are primarily determined by the surface properties (either structural or electronic), as demonstrated by the increased \( k^0 \) for \( \alpha \)-Fe\( _2\)O\( _3 \) after platinization of its surface.2 Platinization of \( \text{WO}_3 \) slightly increases the et kinetics. However, the reductant material, \( \text{H}_2\text{WO}_3 \), has a smaller \( k^0 \) than \( \text{WO}_3 \). Thus it appears that platinization must increase the interfacial kinetics, which compensates for the slower kinetics from the reduction (since the platinization of \( \text{WO}_3 \) also causes it to be reduced).

From the slopes in Figure 4, \( \alpha \) is calculated and is listed in Table I. The values for the transfer coefficient are significantly greater than 0.5, as was also found for the iron oxides.2

Conclusions

Electrochemical studies of irradiated \( \text{WO}_3 \) after different treatments in the absence and presence of a mediator provide information about the Fermi level for electrons and et kinetics. Platinization of \( \text{WO}_3 \) results in irreversible reduction and a shift in \( nE_F^* \) in a negative direction, as does direct reduction of \( \text{WO}_3 \) in an \( \text{H}_2 \) atmosphere. Monolayer \( \text{WO}_3 \) on silica displays an \( nE_F^* \) of about 170 mV negative of that for bulk \( \text{WO}_3 \) and an increase in band gap, perhaps due to quantum effects. Examination of photocurrent transients for direct et to the electrode at large overpotentials suggest that the particles stick to the electrode surface. Tafel plots can be constructed for the determination of the heterogeneous et rate constant, \( k^0 \). Reduction of \( \text{WO}_3 \) decreases \( k^0 \), while platinization increases \( k^0 \) slightly.

Acknowledgment. We gratefully acknowledge the support of the National Science Foundation (CHE8304666). We thank T. Varco-Shea for performing the XPS measurements.

Adsorption of NO on Ni(755): Competitive Adsorption of Oxygen and Nitrogen Atoms along a Step Line of Ni(755)

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The adsorption of NO on Ni(755) was studied by means of temperature-programmed desorption (TPD) and Auger electron spectroscopy (AES). A peculiar behavior of TPD spectra for N\( _2 \) can be explained by a competitive adsorption of oxygen and nitrogen atoms along a step line of Ni(755). The adsorption energy of oxygen atoms along a step line is higher than that of nitrogen atoms.

One of the main efforts in the science of catalysis is to clarify the structure of active sites. For many catalytic reactions, step sites are considered to be active sites.1 However, there are rather few studies about chemical modifications of step sites and the