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OBSERVATION OF OXYGEN ADSORPTION
ON MOLYBDENUM TRIOXIDE BY FIELD
ELECTRON EMISSION TECHNIQUE

By

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Abstract

The FEM image of adsorbed oxygen on an oxidized surface of molybdenum was observed as a bright "fourfold clover-leaves" spot. Besides the Fermi peak, two extra peaks were detected in the FEED spectra for this spot at 1.2 eV and 1.7 eV below the Fermi level. These extra peaks were attributable to the inelastic interactions of tunnelling electrons with the adsorbed molecular oxygen.

Introduction

Field electron emission microscopy (FEM),[1] with its large magnification and high resolution, has already made significant contributions to our knowledge of molecular processes[2] involved in adsorption phenomena and chemical reactions on some metal catalyst surfaces.[3] Especially, by means of the probe hole technique,[4] the FEM study on a single-crystal face of the metal tip surface has provided quantitative information. Furthermore, the spectroscopy of the total energy distribution of field emission (FEED)[5] is expected to give information upon the electronic characteristics of the surface of both metal and metal oxide catalysts.[6] The present work is concerned with the FEM patterns and FEED spectra of adsorbed oxygen on an oxidized surface of molybdenum, which is known to be an active catalyst for the partial oxidation of methanol.[7]

Experimental procedure and results

A clean surface of a Mo-tip in the FEM cell was subjected to heat treatment at 1000 K in ambient oxygen of $\sim 10^{-5}$ Torr for several minutes, high tension being applied to the tip simultaneously. The heat treatment

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resulted in the growth of MoO_3-clusters[6,8] on the tip surface, as the FEM pattern of Fig. 1 indicates. It was found that remoulded granular MoO_3-clusters were prominent on the {111} planes of the tip surface. This built-up surface was exposed again to oxygen of about 10^{-3} Langmuir at room temperature and evacuated at about 650 K in a furnace. In the emission pattern, superposed on the less bright main pattern shown in Fig. 1, stationary bright spots appeared. They were disks, doublets and quadruplets,[9] typical examples being shown in Fig. 2. These spots vanished from sight at once by heat treatment of the tip at 800 K, which suggests the desorption of adsorbed species at that temperature.

The observation of FEED spectra was carried out for a quadruplet or a "fourfold clover-leaves" spot. The experimental setup is shown schematically in Fig. 3. The FEM cell in Fig. 3 consists of an emitter tip assembly, a quartette of electrostatic deflection electrodes, and a retarding potential analyzer of the van OOSTROM type[10] which is made up of an anode, lens-electrodes and a hemispherical Faraday cup. The tip assembly can be shifted slightly by means of a bellows arrangement so that a paraxial emission beam is obtained. The analyzer is designed in such a way that electrons passing through a 1-mm ϕ probe hole at the center of anode are focussed by the two lens-electrodes, go through central probe aperture holes on the electrodes, and are finally collected on the Faraday cup. This retardation analyzer gave a resolution[11] of about 80 mV and a signal-to-noise ratio of 40 dB. The deflection electrodes made of molybdenum sheets are mounted close to the emitter tip and appropriate potential was applied to each pair of the *vis-à-vis* sheets. These electrodes allowed to bring any desired region of the field emission pattern over the probe hole and also to correct some deformation of the shape of the quadruplet image.

The size of the quadruplet image on the screen, several millimeters squared, was larger than that of the probe hole, one millimeter squared, so that each bright leaf of fourfold clover-leaves covered the prove hole. In the result, among the field-emitted electrons from the tip having sufficient total energy to pass through the anode, only a small portion of them arrived perpendicularly to the surface of the Faraday cup collector. Figure 4 shows the block diagram of the electric measurements. The retarding voltage applied to the tip and biased against the collector was modulated by a superimposed signal of 70 mV_{p-p} and 270 Hz. Thus the probed electron beam was differentiated by a lock-in amplifier. Then, the energy distribution spectra of $\log \dfrac{dj(\varepsilon)}{dE}$[5] *vs.* E were plotted on an x—y recorder, where ε is

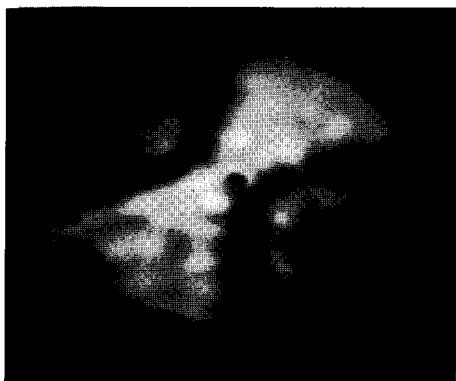*Oxygen Adsorption on MoO₃ by Field Electron Emission Technique*

Fig. 1. Spotty and bright MoO₃-clusters, caused to develop on a clean Mo-tip surface under the conditions, $T = 1000$ K, $P_{0_2} = \sim 10^{-5}$ Torr and negatively applied high field of about 3×10^7 V/cm. In this plate, the probe hole of 1-mm ϕ in the screen is visible at the constricted part of the bright region, prominently around the {111} planes, which is a throng of granular MoO₃-clusters.
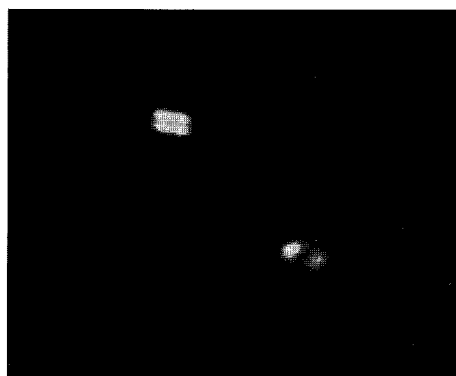

Fig. 2. Clear-cut images of both the doublet and quadruplet spots.

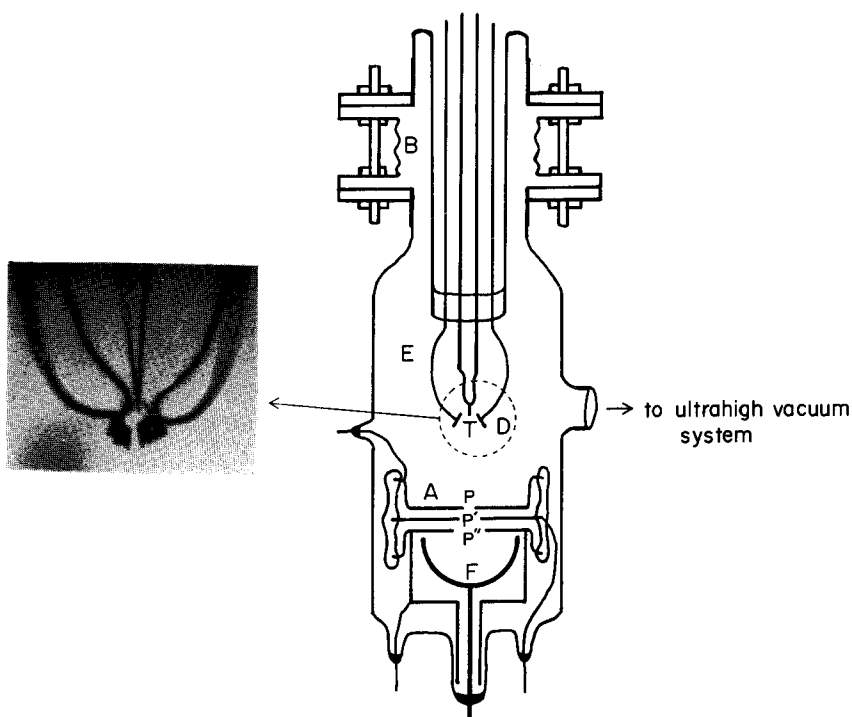

to ultrahigh vacuum system

Fig. 3. A schematic diagram of the experimental setup. B: bellows arrangement, E: emitter tip assembly, T: Mo-tip, D: two pairs of deflection electrodes, A: van Oostrom type analyser, P: 1-mm ϕ probe hole in the anode (screen), P′ and P″: 2-mm ϕ and 4-mm ϕ probe holes in the lens-electrodes, F: Faraday cup.
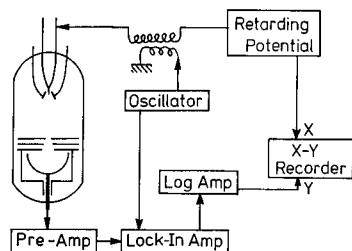
Fig. 4. The block diagram of electric measurements.

$E-E_F$, E is the potential of the collector, E_F is the Fermi level of molybdenum oxide and $J(\varepsilon)$ was the observed current per unit total energy as a function of ε. The FEED spectrum of the quadruplet image, *i. e.*, that of any one of the four leaves, at room temperature is shown in Fig. 5.

The facts observed in the spectrum are as follows : (1). Two extra peaks besides the Fermi peak were detected at 1.2 eV and 1.7 eV below the Fermi level (E_F) respectively. (2). These two peaks shifted little with the increase of the applied field. (3). Any of the four leaves gave the two extra peaks and the Fermi peak of the same heights respectively. (4). The ratio of the height of each extra peak to that of the Fermi peak was almost independent of the field, *i. e.*, nearly constant.

Fig. 5. The FEED spectrum for any one leaf of the fourfold clover-leaves image logarithm of state density $\left(\log \dfrac{dJ(\varepsilon)}{dE} \right)$ *vs.* potential (E).

E_F: the Fermi level of molybdenum trioxide, E: the potential of the Faraday cup, $J(\varepsilon)$: the observed current per unit energy relative to the E_F, $\varepsilon = E - E_F$. In each spectrum, besides the Fermi peak at 0 eV, two extra peaks, *i. e.*, a prominent peak at -1.2 eV and a hump on the shoulder of the -1.2 eV peak at -1.7 eV are observed.

Discussion

Supposing that the adsorbed oxygen molecules on the tip surface are not dissociated, we may interpret the observed results in the following way.

a) In the FEM observation, when an oxygen molecule is adsorbed on a ridge of an uneven surface of MoO_3-cluster, this protuberance on the surface
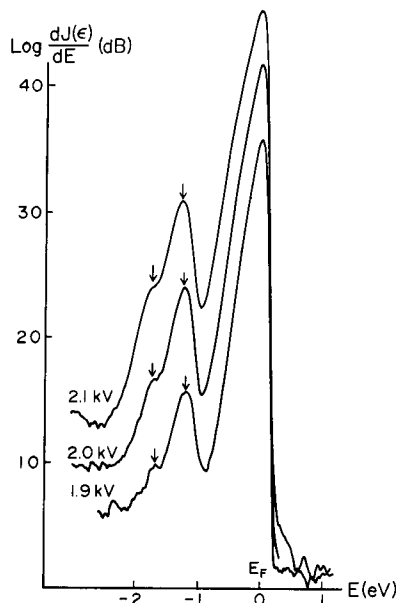
distorts and compresses the equipotentials in its vicinity and causes local field enhancement, resulting in considerably higher local magnification[12] of its image on the anode screen on account of the lens effect.[1,13] Thus in spite of the small size, an oxygen molecule will be able to show up clearly as a bright spot. The observed shape of the spot is a disk, a doublet or a quadruplet image[1,14] and, in this work, the authors treated of only a quadruplet, fourfold clover-leaves image. In the FEED spectrum for each of the individual leaves the two characteristics of extra peaks were quite the same, respectively, as described in the results (1) to (4). Thus it is presumed that one oxygen molecule adsorbed on the tip surface corresponds to the one quadruplet image on the screen.

b) These extra peaks for the adsorbed oxygen molecule on the tip surface may be attributed to either the resonance tunnelling[15] of electrons from the tip or the inelastic tunnelling.[16] The former arises from the electronic state of an adsorbed oxygen molecule near the Fermi level and for each spectrum, in this case, the ratio between the heights of the extra peak and of the E_F peak changes with the applied field.[17] As for the latter, electrons at E_F level lose so much energy to excite the electronic or vibronic state of an adsorbed oxygen molecule and in the energy loss spectrum, the ratio between peak heights changes little with the field.[17] The result (4) for the case of the individual leaves of the quadruplet image is likely caused by the latter. The energy levels of the 1st and the 2nd excited states ($^1\Delta_g$ and $^1\Sigma_g^+$) above the ground state ($^3\Sigma_g^-$) of the adsorbed oxygen molecule are estimated at about 1 eV and 1.6 eV respectively,[18] which are nearly equal to the values of the result (1). Provided that these excited states are hardly affected by the applied field, the peaks in the energy loss spectrum will not shift with the field, in agreement with the result (2).

Among researches on the subject of gas adsorption on a metal tip surface associated with the inspection of field emission image, as far as we are aware, several ones of large molecules, such as copper phthalocyanine *etc.*, are reported in the literature[17,19] and few of small molecules, such as oxygen. In this report, the above-mentioned interpretation, which is based on the model of an oxygen molecule adsorbed on the steep ridge of a MoO₃-cluster, qualitatively fits in with the experimental fact of the extra peaks, although each of the peak height is much larger than the theoretical value,[16] based on an adsorbate upon the even plane of the surface. Now, more detailed investigations are needed, from both the experimental and theoretical points of view, to understand inelastic tunnelling of electrons through the adsorbed oxygen molecule on the tip surface and to derive information on the situation

of field emission images of adsorbed oxygen.

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