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NOTES

Evidence for Short-Range Order and Steps in MoO_3 Crystal Surfaces

The structural characterization of solid surfaces by LEED and other techniques has led to important advances in the field of catalysis (*1*). Other techniques like electron diffraction in the microscope were traditionally used as "bulk" techniques until recently, but now it has been incorporated as a powerful tool for assessing the crystal surface features such as steps and roughening down to atomic height dimensions (*4, 5*). The systematic application of this method for the characterization of continuous Au films and particles allowed some authors to recognize single atomic steps on thin film surfaces (*2, 4*). Other materials like the metal oxides and sulfides, commonly used as oxidation and dehydration test catalysts, are also suitable for surface characterization by electron microdiffraction techniques.

The aim of this note is to provide evidence for surface features occurring in MoO_3-test catalysts which were found by microdiffraction methods. The results should be of relevance for establishing a correlation between catalytic selectivity and surface structure in oxidation and dehydration reactions of hydrocarbons (*6*), where a structure sensitivity behavior has been claimed (*9*).

Once the microdiffraction pattern from a very small crystal area of about 200 Å diameter is obtained, the method consists in searching for the special extinction conditions which arise from the incomplete filling of the uppermost unit cell, that is the crystal surface. For the orthorhombic MoO_3 crystal system and considering an integer number of unit cells (N) along [010] direction, the structure factor is null for the reflections (100) and (001), i.e., the spatial-group forbidden reflections. However, if the upper or lowermost crystal unit cell is not complete, the structure factor is not null because, in this case, there is an extra term: $F_{hkl} = F'_{hkl} + F''_{hkl}$, where F'_{hkl} is the structure factor for N complete cells and F''_{hkl} is the corresponding structure factor for a fraction of unit cell.

The corresponding scattering amplitudes were calculated for each reflection from atomic positions reported elsewhere (*3*). For each layer inside the unit cell the total structure factor, F_{hkl}, was evaluated at intervals of one-, two-, three-, and four-fifths of unit cell along *b*-axis. The choice of this fractional series is dictated by the structure itself, because each fraction corresponds to nearly a Mo atom position along the cell height. For those intervals the structure factor was determined and the relative ratios of scattering intensities were calculated. Other calculations for MoO_3 thin crystals were carried out by some authors (*15*) using multislice methods, but those considered only intervals of one-half of unit cell; the present calculations extend those reported previously and provide a systematic approach to map crystal surfaces under the crystal dimensions.

The intensity ratio calculated in this work are condensed in Table 1. As observed, both (100) and (001) type reflections must appear simultaneously for steps of 1/5 *b* and 4/5 *b* height, while for the 2/5 *b* and 3/5 *b* only (100) type reflections must be visible. Finally, for one complete unit cell the total extinction condition is recovered.

A series of selected area and microdiffraction patterns taken from large areas of 1

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TABLE 1

Alternate Appearance of the (100) and (001) Reflections as Function of Crystal Thickness for 1/5 *b*, 2/5 *b*, 3/5 *b*, 4/5 *b*, and 1 *b* Unit Cell

Relative intensity ($\times 10^4$)	Thickness (along *b* axis)				
	1/5 unit cell	2/5 unit cell	3/5 unit cell	4/5 unit cell	1 unit cell
I_{100}/I_{200}	392	2	4	6312	0
I_{001}/I_{200}	404	0	0	6469	0

μm diameter and from very small areas of 200 Å diameter, respectively, showed the typical symmetry depicted in Fig. 2. That is the [010] reciprocal zone of MoO_3 which contains both allowed ($h,l = 2n$, for $h00$ and $00l$ type reflections) and (100), (001) type forbidden reflections simultaneously, which might correspond to the 1/5 b or 4/5 b step height noted in Table 1.

Those patterns were taken from MoO_3 crystals which were prepared by sublimation and condensation of Mo powder (*11*). The crystallographic parameters of the MoO_3 crystals agreed with other reports (*6*, *7*) and the typical crystal habit is illustrated in Fig. 1.

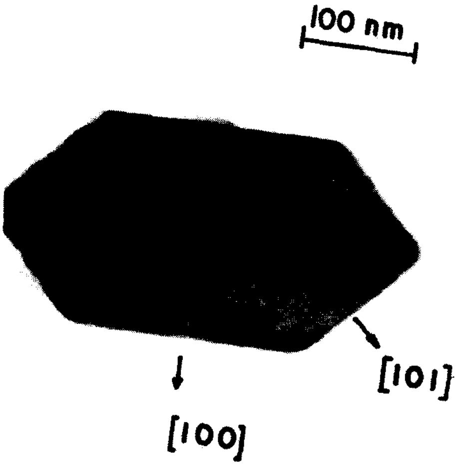

FIG. 1. Typical MoO_3 crystallite with habit planes.

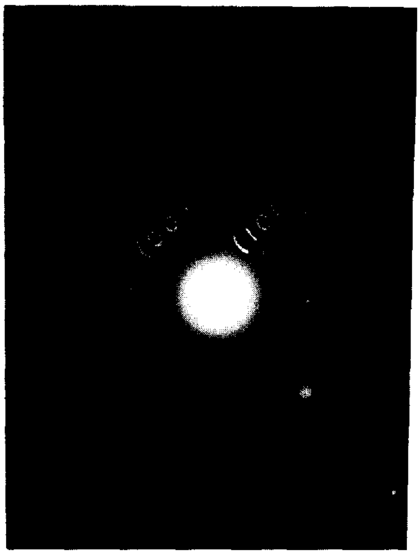

FIG. 2. Typical electron diffraction pattern in [010] zone. Forbidden reflections, i.e., (100) and (001) are clearly outlined.

A series of tilting experiments was realized to verify that the forbidden reflections (100) and (001) were not double diffraction spots. Instead, those are long rods in reciprocal space, associated to the very thin crystal layer that modifies the structure factor as mentioned above, that is the top incomplete unit cell of the crystal (*4*, *5*).

Upon further irradiation in the electron microscope, it was found that both (100) and (001) surface reflections split up as shown in Fig. 3. Furthermore, the diffuse split reflections around the (100) and (001) positions do not vanish upon tilting up to ±30 degrees, but, instead, their intensity is little modified in comparison with the allowed reflections, which disappear completely. This result confirms the surface character of those diffuse reflections too. More similar results were obtained using an electron beam of less than 200 Å diameter, confirming that diffuse split reflections may arise too from very small crystal areas. In addition, several extinction conditions noted in Table 1 were also obtained from

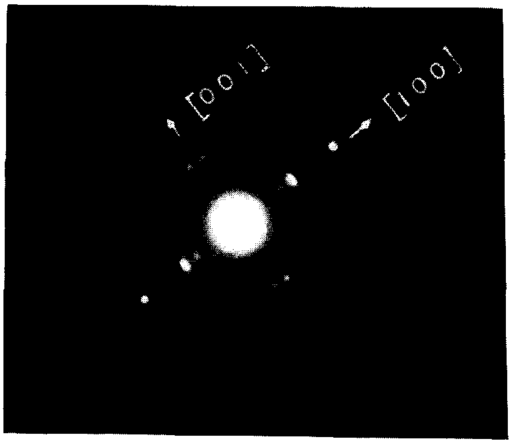

FIG. 3. Electron diffraction pattern taken after some minutes of electron beam irradiation. The (100) and (001) reflections split into diffuse "brackets."

those microdiffraction patterns that will be reported in a forthcoming publication.

On the other hand, the occurrence of diffuse "brackets" around the extra reflections in electron diffraction patterns (as, for example, in superlattice reflections), was observed above critical temperatures in other solid binary systems like IT-TaSe (*8*). Those features seem related to the short-range ordering and variations of the Fermi surface, that is a combination of both geometric and electronic effects. Therefore, the question arising from the present results (Fig. 3) is whether the diffuse scattering "brackets" around (100) and (001) positions were due to electronic effects arising from the crystal bulk or from geometric arrays on the MoO_3 crystal surface. In order to rule out one of those possibilities, several experiments based on simulation and surface modeling in a laser optical diffractometer were carried out. The method consisted in taking several two-dimensional models and using them as diffraction gratings to obtain the power spectrum, that is the optical transform. The aim of this series of experiments was to prove whether or not diffuse "brackets" around some of the main reflections could be obtained only from the geometric 2-D models, which should demonstrate that the electronic effect does not play any role. One of the best fittings is shown in Figs. 4a and b, where one observes the power spectrum and its corresponding model. It is clear that diffuse "brackets" may originate from thin periodic objects which have a certain disorder degree, that is a short-range ordering plus a plane distortion.

Other investigations on MoO_3 crystal surfaces by LEED techniques found that, though a substantial disorder coexisted

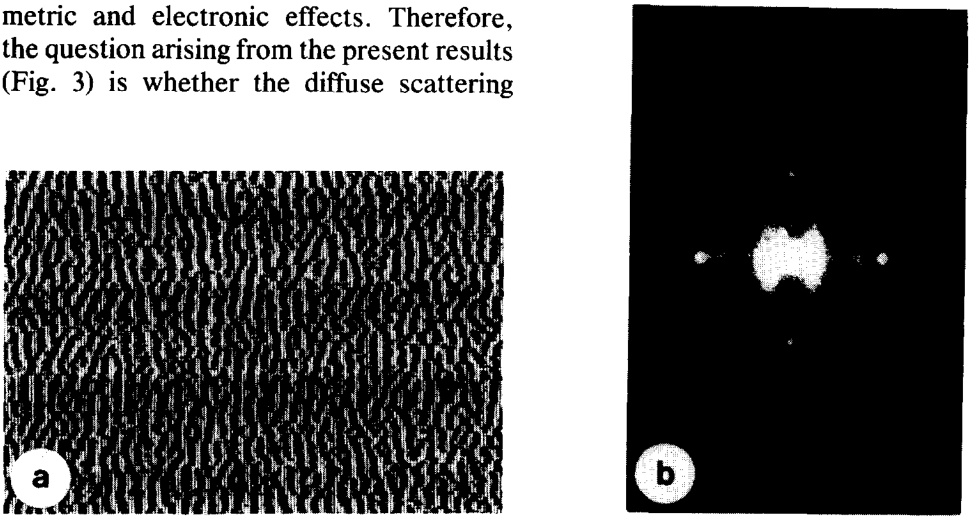

FIG. 4. (a) Geometric model used as diffraction grating. The weaving planes are clearly observed. (b) Optical transform, i.e., power spectrum, of the model above. Diffuse scattering around reflections are clearly outlined.

with ordered surfaces, the unit mesh at the MoO_3-(010) surface remained unchanged (*12*). Also, evidence for an homologous series of shear structures based on MoO_3 was detected by additional spots, streaks, and satellites around the main reflections in the electron diffraction patterns (*9, 11, 13*). A key feature of the MoO_3 structures is the ability to undergo shear transformations through slight changes in the Mo/O ratio (*10*); however, the initial crystals for the present case did not show extra features (Fig. 2), suggesting that crystallographic shear (*CS*) was absent initially, but surface steps were present. The subsequent irradiation of MoO_3 crystals under the vacuum conditions of the microscope led first to spliting of the surface reflections (Fig. 3) and, lately, to streaking of the "bulk" type reflections (200) and (002). The splitting effect was demonstrated to be related to surface disorder due to electron bombardement, while streaking (*14*) of the "bulk" reflections was most probably related to the development of planar defects of *CS* type. A clear distinction is then made between both surface and bulk effects, through the analysis of the electron microdiffraction patterns. The main evidence is that splitting, i.e., surface disorder, occurs first than streaking (i.e., planar faults inside the crystal bulk), thus ruling out the possibility that the surface features here described were due to crystallographic shear from the bulk.

In conclusion, it was demonstrated that single MoO_3 crystals, commonly used as oxidation and dehydration test catalysts, have a thin surface layer formed by an incomplete unit cell. There is evidence for steps of different height (see Table 1) along *b* axis, at least. The surface sites, associated with such surface arrays, could be rather different than those derived from assumptions based on smooth surfaces, making it that catalytic properties be dependent on the statistical distribution of those surface arrays and steps. Finally, upon thermal heating or electron beam irradiation the original surface is modified, then new surface arrays are developed which are consistent with the model of weaving planes having a short-range order component. Other studies on the site type distribution on (010) type surfaces should be possible by microdiffraction techniques which will be reported soon.

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