



Crystallographic Shear Defect in Molybdenum Oxides: Structure and TEM of Molybdenum Sub-oxides $\text{Mo}_{18}\text{O}_{52}$ and Mo_8O_{23}

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Abstract

Molybdenum trioxide and molybdenum sub-oxides are of great interests in catalysis due to their utilities as model system to elucidate the correlations between the structure and the catalytic performance. The sub-oxides are usually an intermediate phase during catalytic reaction in which the lattice oxygen is involved. We show the identification of the two common molybdenum sub-oxides $\text{Mo}_{18}\text{O}_{52}$ and Mo_8O_{23} , derived from MoO_3 by crystallographic shearing (CS), by means of electron diffraction and High-Resolution Transmission Electron Microscopy (HRTEM) in combination with image simulation. The coincidence of simulated electron diffraction patterns and high-resolution images with the experimental ones indicates the feasibility of CS structure determination by these techniques.

Keywords: molybdenum oxides, crystallographic shear, electron diffraction pattern, high-resolution electron microscopy, image simulation.

Introduction

Molybdenum oxide based catalysts are extensively employed for partial oxidation of alkenes both in industrial application and in academic research. The reaction may proceed with interaction between species of chemisorbed hydrocarbon and oxygen by the so called Mars-van Krevelen mechanism, according to which the oxidation proceeds in two stages: (a) reduction of the catalyst with a hydrocarbon at the expense of the catalyst oxygen, which is incorporated into the products, and (b) re-oxidation of the reduced catalyst by gaseous oxygen. Recently it has been reported that not only the surface, but also the bulk structure of the catalysts is involved in the oxygen insertion process [1, 2]. For molybdenum oxides, consisting of MoO_6 octahedra as their basic structural unit, the removal of oxygen species introduces considerable structural rearrangement. One of the ways in which oxides can accommodate such changes includes the well documented CS defect process. The CS essentially eliminates planes of anion vacancies by shear from corner to edge sharing of octahedra and the crystal collapse

of the oxide, and therefore generates extended CS plane defects.

Superlattice of oxygen vacancies in MoO_3 has been observed during thermal treatment in the electron microscope at higher temperatures and the oxygen vacancies were proposed to be consumed in the production of CS planes [3]. Furthermore, at early stages of MoO_3 reduction using H_2 , CO or propene at temperatures varying from RT to 600°C, partial screw dislocation in $\{101\}$ planes bounding a stacking fault extending from the surface, partial edge dislocation with Burgers vector $\mathbf{b}=[a/2, b/7, 0]$ forms on the surface. These reduction-induced defects can cause the lattice collapse and are consistent with crystallographic shear [4-6]. One consequence of the defect formation can be the formation of a short range ordered structure which was suggested to be " $\text{Mo}_{18}\text{O}_{52}$ " type crystallographic shear, as it was found by the recent in situ XAFS during TPR of MoO_3 in 10 vol % propene from 300 K to 773 K. The similar results were also obtained during the oxidation of MoO_2 in oxygen [7]. Electron paramagnetic resonance study of interactions between

MoO₃ and propene confirms the formation of shear structures following desorption of the oxidized organic molecule [8].

It is therefore clear that defects and defect formation play an important role in the red-ox process of molybdenum oxides, but the question, whether the defects are the driving force for the catalytic reaction or its by-products, is still open. In searching for the answers to the question, we have to first of all study the structure and formation of sub-oxides that are believed to act as an intermediate phase in cluster form during the red-ox process of the catalysts. In the present work, two representative molybdenum sub-oxides with CS structure, Mo₁₈O₅₂ and Mo₈O₂₃ are studied crystallographically in aspect of the formation. By matching the experimental high-resolution images and diffraction patterns with simulated ones, the CS structure determination can be achieved unambiguously. This also shows that the HRTEM technique combined with simulation can be applied to structure determination for other molybdenum oxides with different degrees of reduction.

Structural principle of molybdenum oxides

As well known, MoO₃ crystallizes in orthorhombic structure (space group Pbnm). It consists of double layers of linked distorted MoO₆ octahedra parallel to (010) plane. In each double layer MoO₆ octahedra form edge sharing zig-zag rows along [001] direction and corner sharing rows along [100] direction. Successive layers are held together by weak van der Waals forces only, with easy cleavage along (010) plane (Fig. 1). Mo₁₈O₅₂ can be derived from the layered MoO₃ structure. It is convenient to project MoO₃ onto

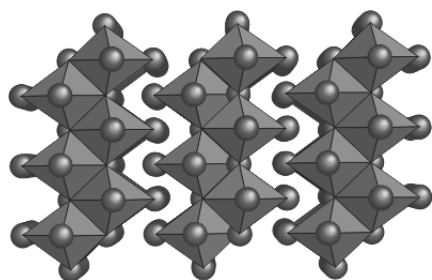
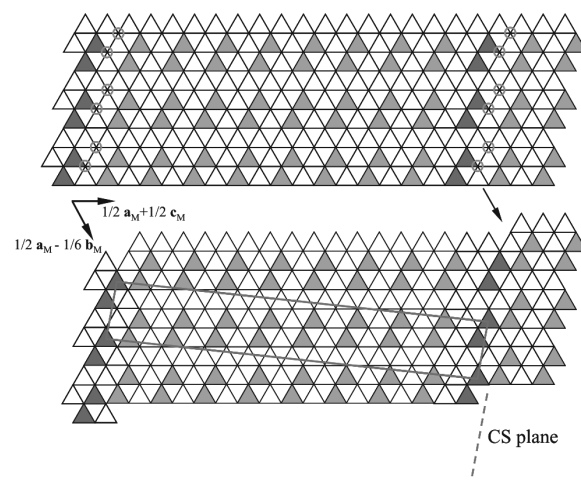
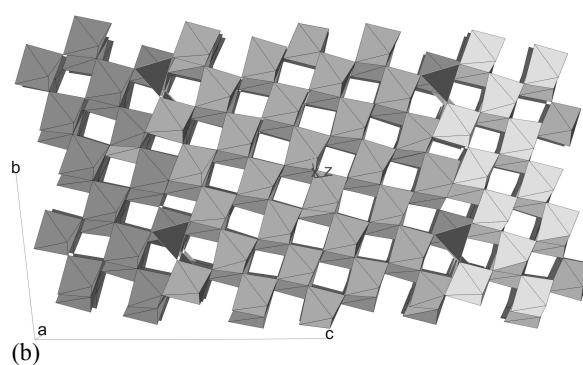


Fig. 1. [100] projected MoO₃ structure model.

(13 $\bar{1}$)_M plane, approximately the close packed plane. The removal of the rows of oxygen atoms from (35 $\bar{1}$)_M plane is accommodated by the crystallographic shear operation along $[1/2\mathbf{a}_M - 1/6\mathbf{b}_M]$, where subscript M denotes the vectors and planes of the MoO₃ crystal [9]. This process is shown in Fig. 2a, where oxygen atoms stand on the point of each triangle and at the center of each dark triangle, one Mo atom is stacked on three oxygen atoms. The removed oxygen atoms are indicated by the circles. The formed Mo₁₈O₅₂ exhibits a triclinic cell and its [100] zone corresponds to the $[\bar{1}12]$ zone of MoO₃. Its [100] projected structure model is shown



(a)



(b)

Fig. 2. Structural principle of Mo₁₈O₅₂. (a) CS planes formation exhibited on (13 $\bar{1}$) plane of MoO₃ and (b) [100] projected Mo₁₈O₅₂ structure model.

in Fig. 2b. The space group of Mo₁₈O₅₂ is $P\bar{1}$ with $a = 8.145 \text{ \AA}$, $b = 11.89 \text{ \AA}$, $c = 21.23 \text{ \AA}$, $\alpha = 102.7^\circ$, $\beta = 67.8^\circ$ and $\gamma = 110.0^\circ$.

The Mo₈O₂₃ is formed by periodic crystallographic shear planes induced along {102} plane of a ReO₃ type matrix (Fig. 3). Thus formed CS planes are characterized by the

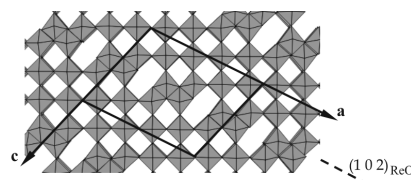


Fig. 3. [010] projected structure model of Mo₈O₂₃.

recurrent occurrence of groups of four edge-sharing MoO₆ octahedra. ReO₃ type blocks are between them, which extend through eight MoO₆ octahedra. The [010] projected unit cell of Mo₈O₂₃ is also outlined in Fig. 3. The space group of Mo₈O₂₃ is P2/a with $a = 13.4 \text{ \AA}$, $b = 4.04 \text{ \AA}$, $c = 13.4 \text{ \AA}$ and $\beta = 106.5^\circ$.

Experimental

The electron diffraction patterns (EDPs) and HRTEM images of single crystal Mo₁₈O₅₂ and Mo₈O₂₃ were taken on a Philips CM200 FEG microscope with accelerating voltage 200 kV, spherical aberration coefficient 1.35 mm and focus spread due to chromatic aberration about 3.0 nm. The models of Mo₁₈O₅₂ and Mo₈O₂₃ were built using routine of “crystal builder” in Cerius package and the atom positions for these two crystals were derived from references [10, 11]. The simulation of EDPs and HRTEM images was carried out using routines of “Diffraction-Crystal” and “HRTEM”, respectively. Multislice method was used for electron propagation in crystal and each subslice did not exceed 2 Å.

Results and discussions

Fig. 4a shows the [100] projected electron diffraction pattern of Mo₁₈O₅₂. The simulated [100] electron diffraction pattern with crystal thickness of 40 Å is shown in Fig. 4b. Both positions and relative intensities of the diffraction spots are similar to each other for experimental and simulated EDPs. The strong diffraction spots arise from the matrix and they coincide with the (110) and (02 $\bar{1}$) diffractions on [$\bar{1}$ 12] zone of MoO₃ (Fig. 4c). Superimposed on the diffractions from the MoO₃ matrix, other weaker diffractions can be attributed to the periodically distributed CS planes parallel to the (001) planes of Mo₁₈O₅₂, which correspond to the MoO₃ (35 $\bar{1}$) planes.

Based on the structure model of Mo₁₈O₅₂, [100] projected, simulated HRTEM images are calculated by Cerius package with crystal thickness from 16.3 Å to 195.5 Å and with focus values from -1400 Å to 900 Å. Part of the simulated image contrasts are reproduced in Fig. 5. The focus step 100 Å and the thickness step 16.3 Å is suitable for exhibiting the distinguishable contrast difference. Figs. 4d and 4e show two HRTEM images of obviously different contrast taken from different areas and with different defocus values. The insets in Figs. 6a and 6b are the simulated images with thickness of 81.5 Å and defocus -400 Å, and that with thickness 32.6 Å and defocus -1000 Å, respectively. The contrast of the simulated images coincides with the experimental ones fairly well. The periodically distributed dark and light areas corresponding to the CS planes can be seen in Fig. 4d, while Fig. 4e shows rather even contrast. However, the diffraction patterns from these two areas are similar to that in Fig. 4a, which indicates the existence of CS planes. Therefore, to reveal CS planes directly in high-resolution images depends on the conditions of image taking and image simulation needs to be carried out for structure determination. Since Mo₁₈O₅₂ keeps the layer structure and the cleavage usually takes place along bc plane, it is convenient to record the EDPs and HREM images on [100] projection and the CS structure can be determined with support of simulation.

Similarly, the [010] projected electron diffraction pattern of Mo₈O₂₃ in Fig. 6a shows the strong diffraction

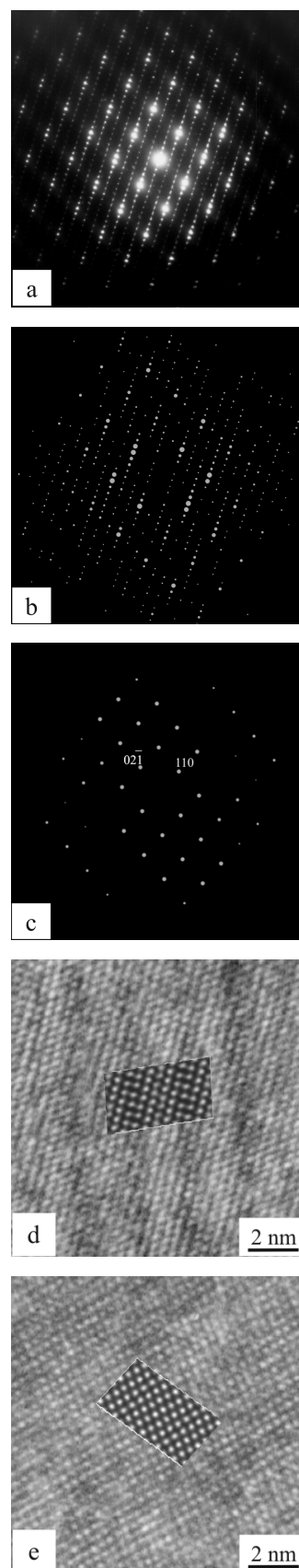


Fig. 4. (a) Experimental and (b) simulated electron diffraction pattern of Mo₁₈O₅₂ on [100] projection; (c) simulated electron diffraction pattern of MoO₃ on [$\bar{1}$ 12] projection; (d) and (e) experimental HRTEM images of Mo₁₈O₅₂ on [100] projection with the simulated images insets.

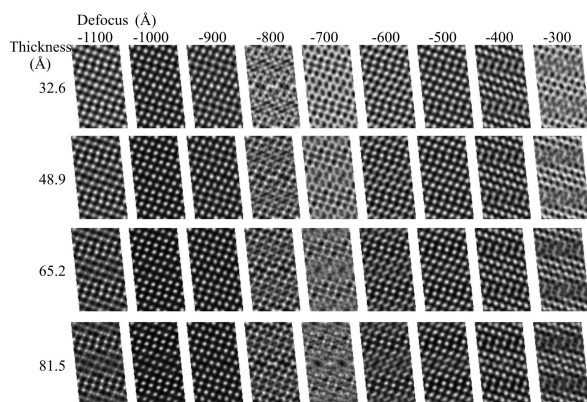


Fig. 5. Simulated HRTEM images of $\text{Mo}_{18}\text{O}_{52}$ with different crystal thickness and defocus values.

spots arising from the matrix with ReO_3 structure and the satellite spots rows from the CS planes. Fig. 6b shows the simulated electron diffraction pattern with crystal thickness 60.6 \AA , which is identical to the experimental one. The corresponding high-resolution image is shown in Fig. 6c and the contrast directly indicates the existence of CS planes. $[010]$ projected simulated images are calculated by Cerius package with crystal thickness from 40.4 \AA to 121.2 \AA (thickness step 20.2 \AA) and with focus values from -1400 \AA to 900 \AA (focus step 100 \AA). Part of the simulated image contrasts are reproduced in Fig. 7. Among them, the image simulated with crystal thickness 60.6 \AA and defocus -100 \AA (inset in Fig. 6c) matches the experimental image best. Another electron diffraction pattern is shown in Fig. 6d. The pattern can be regarded as a mirror reflection of that in Fig. 6a and the projection is deduced to be $[0\bar{1}0]$ direction. Corresponding high-resolution image together with the inset of simulated image with thickness 60.6 \AA and defocus -700 \AA is shown in Fig. 6e. For Mo_8O_{23} , $[010]$ or $[0\bar{1}0]$ projected EDPs and HREM images are suitable for CS structure determination since the characteristic can be easily distinguished in either of them.

Summary

$\text{Mo}_{18}\text{O}_{52}$ and Mo_8O_{23} can be derived from MoO_3 structure by different CS mechanisms. Our studies show that CS plane, which is important in understanding the oxygen diffusion and phase transition mechanism of transition metal oxides during catalytic reactions, produces well defined satellite spots in the electron diffraction pattern. This facilitates the application of TEM techniques for the investigation of the reaction mechanism in solid state chemistry. For $\text{Mo}_{18}\text{O}_{52}$, the CS plane in (001) plane, which is equivalent to $(35\bar{1})$ plane of MoO_3 , produces regular spots on $[100]$ projection, and for Mo_8O_{23} , the CS plane in (001) plane, which is equivalent to (102) plane of a ReO_3 structure, produces regular spots on $[010]$ projection, in the corresponding

diffraction patterns. High-resolution imaging, taken along the proper crystallographic direction and supported by image simulation, allows the visualization of the CS structures at nano scale. This opens the possibility for in-situ HRTEM investigations of the reaction mechanisms under real catalytic conditions at atomic scale.

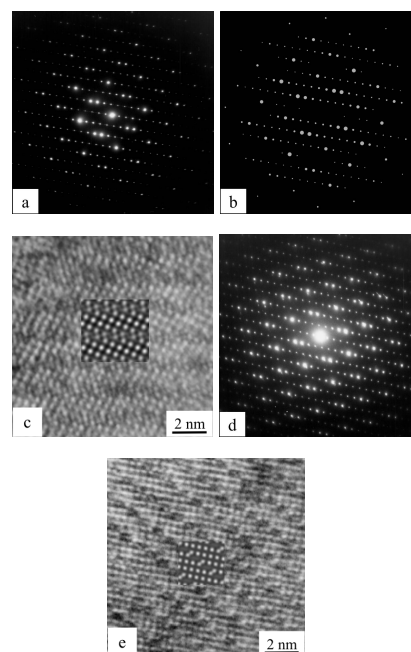


Fig. 6. (a) Experimental and (b) simulated electron diffraction pattern of Mo_8O_{23} on $[010]$ projection; (c) experimental HRTEM image of Mo_8O_{23} corresponding to (a) with the simulated image inset; (d) experimental electron diffraction pattern of Mo_8O_{23} in $[0\bar{1}0]$ projection; (e) experimental HRTEM image corresponding to (d) with the simulated image inset.

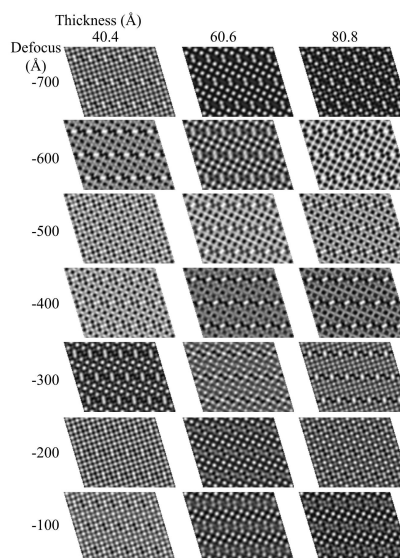


Fig. 7. Simulated HRTEM images of Mo_8O_{23} with different crystal thickness and defocus values.

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