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T. Tanaka, H. Aritani, S. Yoshida, K. Eda, N. Sotani, et al.. Structural Analysis of Molybdenum Bronzes. Journal de Physique IV Proceedings, 1997, 7 (C2), pp.C2-1143-C2-1144. 10.1051/jp4:19972164 . jpa-00255228

HAL Id: jpa-00255228

<https://hal.science/jpa-00255228>

Submitted on 4 Feb 2008

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Structural Analysis of Molybdenum Bronzes

T. Tanaka, H. Aritani, S. Yoshida, K. Eda, N. Sotani and S. Hasegawa

Department of Molecular Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan

Abstract. Hydrogen molybdenum bronzes, $H_{0.21}MoO_3$ (type I) and $H_{0.91}MoO_3$ (type II) were characterized by Mo K-edge XAFS spectroscopy. XANES spectra showed that type I has an axially symmetric MoO_6 unit which is mainly connected to each other with vertices sharing and a MoO_4 unit in type II are similar to that in MoO_3 . EXAFS spectra suggested that the MoO_x sheet in type I is similar to MoO_3 while in type II, a MoO_x sheet is similar to that in rutile MoO_3 in which MoO_6 is connected to form a chain by sharing the edges of opposite sides. The curve fitting analysis of Mo-O bonds for type I supported the earlier results obtained from diffraction and IR methods; a MoO_6 unit has C_{4v} symmetry. In case of type II, D_{4h} structure is possible and hydrogen is captured by $Mo=O$ bonds resulting in the formation of Mo-OH bonds.

1. INTRODUCTION

Hydrogen molybdenum bronze, H_xMoO_3 , is classified to four phases depending on included hydrogen [1]; type-I (orthorhombic) $0.21 < x < 0.4$ [2], type II (monoclinic) $0.85 < x < 1.04$, type III (monoclinic) $1.55 < x < 1.72$ and type IV (monoclinic) $x = 2$. Type I has a layered structure in which a layer consists of two MoO_x sheets. The MoO_6 units connecting to each other with vertices (corner) sharing in the sheet have been proposed to be in an axially symmetric moiety deduced from the result of infrared absorption (IR) [3,4] and 1H NMR studies [5]. The other monoclinic phases are not fully characterized. The present paper is devoted to analysis of the local structure of hydrogen molybdenum bronzes types I and II by means of Mo K-edge XAFS spectroscopy.

2. EXPERIMENTAL

Types I and II were prepared by reduction of MoO_3 in an acidic media according to the Glemser's method [1]. The formation of types I and II are confirmed by XRD [1] and the hydrogen contents were $x = 0.21$ and $x = 0.91$, respectively [3].

XAFS spectra were taken by EXAFS facility installed on BL-10B at Photon Factory (ring energy 2.5 GeV and stored current 360-270 mA) in National Laboratory for High Energy Physics, Tsukuba (Proposal No. 94G002) with a Si (311) channel cut monochromator. The data reduction was performed [6] at the Data Processing Center of Kyoto University.

3. RESULTS AND DISCUSSION

3.1 XANES spectra

Figure 1 shows normalized XANES spectra of the samples and some reference complexes.

For XANES spectrum of type I, the pre-edge peak due to $1s$ to $4d$ transition is seen and the intensity is almost the same as that of $MoO_2(acac)_2$ with D_{4h} symmetry, in which four O atoms from acetylacetonato groups are located at square apexes and two O atoms of molybdenyl are at the vertical axis. The pre-edge peak intensity is lower than that of MoO_3 in which a Mo ion is located at the center of a much distorted oxygen octahedron, indicating that Mo ions in type I is located at the center of highly symmetric moiety. Twin peaks at post-edge regions are found at the similar positions to that found in the case of $MoO_2(acac)_2$ although the intensities are slightly different. This is possibly due to the positions of axial O atoms as Sotani *et al.* reported [2, 3]; i.e., in type I with C_{4v} symmetry, one O at an axial position is of a $Mo=O$ bond and the other is a bridging oxygen. On the other hand, the spectrum of type II is totally similar to that of MoO_2 of rutile structure. The pre-edge peak for MoO_2 was almost missing this is mainly due to

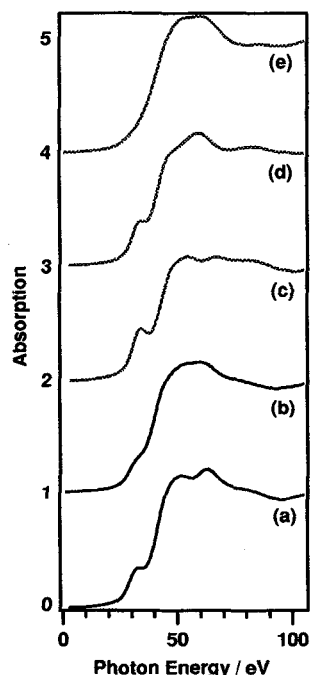


Figure 1 Normalized Mo K-edge XANES Spectra of (a) type I, (b) type II, (c) MoO_3 , (d) $MoO_2(acac)_2$, and (e) MoO_2 . Energy offset is taken to be 19960 eV

the valence of Mo in an axial symmetry. The weak shoulder peak due to $1s$ to $4d$ transition for type II reveals that Mo is located at a more symmetric center than that of type I and/or Mo is partly reduced from hexavalence. Type II, $H_{0.91}MoO_3$, has a molybdenum ions the formal charge of which is almost $5+$.

3.2 EXAFS Spectra

Figure 2 shows Fourier transforms of k^3 -weighted EXAFS spectra. The peaks found in a region $1-2 \text{ \AA}$ are due to the scattering from adjacent O atoms in all spectra. As found in the cases of MoO_2 and $MoO_2(acac)_2$, the complex with small divergency of Mo-O bonds exhibits intense peaks. From this point of view, Mo-O divergency is high in the cases of types I and II. The peaks found at $2-4 \text{ \AA}$ are due to the scattering from adjacent Mo atoms. In case of MoO_3 , MoO_6 units are linked with edges and vertices sharing and the nearest Mo-Mo distances are diverging resulting in the weak intensities in the region $2-3 \text{ \AA}$. Therefore contribution of Mo-Mo scattering is mainly due to the adjacent Mo ions in MoO_6 unit connecting with vertices sharing. This type of MoO_x sheet is similar to that of type I. On the other hand, MoO_2 of a rutile structure has a regular Mo-Mo atomic distances 2.51 and 3.51 \AA , which is reflected to twin Mo-Mo peaks in the region $2-4 \text{ \AA}$. The same feature can be seen for the case of type II, suggesting that MoO_6 unit in type II is connected to each other with not only vertices sharing but also edge sharing as found in the rutile structure.

Table 1 Curve fitting results of Mo-O in the sample

sample	CN	R / \AA	$\Delta\sigma^2 / \text{\AA}^2$	Refinement
type I	0.6(5)	1.64(1)	0.0019(6)	3.6 %
	4.1(4)	1.97(2)	0.0027(4)	
	1.0(5)	2.40(2)	0.0027(4)	
type II	1.5(5)	1.84(1)	0.0021(8)	8.6 %
	3.9(5)	2.01(1)	0.0055(7)	

The empirical parameters from K_2MoO_4 were used. The values in parentheses are standard deviation. $\Delta\sigma^2$ is the relative Debye Waller factor.

The curve fitting analysis was carried out [6] for the Mo-O bonds and the result are given in Table 1. In case of type I, the presence of three kinds Mo-O was concluded. The shortest is possibly due to $Mo=O$ which faces to the interlayer and four O atoms are located in the sheet. The longest is due to the O atoms at the opposite vertex of $Mo=O$. The result is well consistent with that deduced from IR analysis [2,3]. In case of type I, two shell fitting gave the satisfactory result. The longer Mo-O bonds are equatorial. The shorter were axial corresponding to $Mo=O$ in type I. The elongation of this bond is caused by the H intercalations resulting in the formation of $Mo-OH$. Therefore, D_{4h} structure for a MoO_6 unit as in the case of $MoO_2(acac)_2$ is very likely. The structure is basically the same as that found in MoO_2 .

From the results mentioned above we concluded the structure of type I and type II as follows. Type I has a layered structure in which MoO_x sheet similar to that in MoO_3 and the MoO_6 unit is more regular symmetric (C_{4v}). This is well consistent with the earlier result from diffraction techniques [1,7,8] and IR [2,3]. In type II, MoO_x sheet is similar to that in MoO_2 in which MoO_6 is connected to form a chain by sharing the edges of opposite sides.

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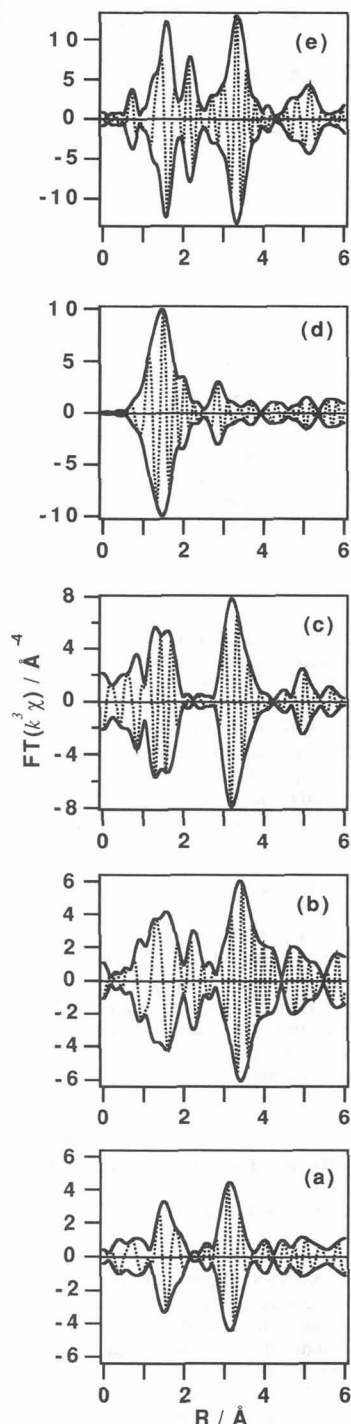


Figure 2 Fourier transforms of EXAFS of Mo compounds. (a)-(e), see captions to Fig. 1