

# Features of Raman band shifts of $\text{MoO}_3$ catalyst exchanged with $^{18}\text{O}$ tracer and active sites for reoxidation

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## Abstract

The oxide oxygens of  $\text{MoO}_3$  catalyst were exchanged with  $^{18}\text{O}$  tracer by a reduction–oxidation method and by a catalytic oxidation of but-1-ene using  $^{18}\text{O}_2$ . The Raman band shifts of the  $\text{MoO}_3$  exchanged with  $^{18}\text{O}$  by the methods were examined. The two bands at 823 and 670  $\text{cm}^{-1}$  of  $\text{MoO}_3$  were shifted to lower frequencies preferentially, while the band of terminal  $\text{Mo}=\text{O}$  oxygen at 998  $\text{cm}^{-1}$  were not shifted very much initially. Applying the correlation between the Raman bands and the stretching modes as described in the literature, the positions of oxide ions and the anion vacancies for reoxidation were estimated. The oxide ions and anion vacancies corresponding to the  $\text{Mo}-\text{O}$  species which have 1.73 and 1.94 Å distances of  $\text{Mo}$  octahedra exhibited rapid diffusions. These anion vacancies also seem to be active sites for oxygen insertion.

## 1. Introduction

The selective oxidation on  $\text{MoO}_3$  catalysts has been studied by many workers. Volta et al. [1] have reported that the (100) plane of the oriented  $\text{MoO}_3$  crystals is responsible for mild oxidation and the (010) plane for total oxidation in propene oxidations. Abon et al. [2] have recently reported that the (120) plane is also responsible for propenal formation in propene oxidation. On the other hand, Jiolkowski [3] has observed that the (010) plane is inactive but the (001) is active for propenal formation. Bruckman et al. [4] have reported that the reactivity of allyl iodide runs parallel with the fraction of

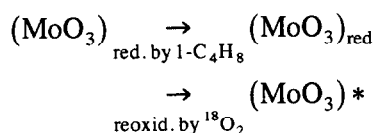
(010) planes where propenal formation occurs. Smith and Ozkan [5] reported that the partial oxidation of methane over  $\text{MoO}_3$  catalysts which exposed different relative amounts of (010) and (100) planes.

According to the previous studies [6,7], the reduction and reoxidation in oxidation reactions take place at different regions over mix oxide catalysts such as Bi–Mo oxides. Previously we have reported that some Raman bands of  $\gamma\text{-Bi}_2\text{MoO}_6$  [8],  $\alpha\text{-Bi}_2\text{Mo}_3\text{O}_{12}$  [8],  $\alpha\text{-MnMoO}_4$  [9] and  $\beta\text{-CoMoO}_4$  [9] catalysts were shifted preferentially to lower frequencies by the exchange with  $^{18}\text{O}$  tracer through a reduction–oxidation method and that, with these oxides, the oxygen uptake seems to take place at the oxygen vacancies corresponding to the bands which were shifted. Smith and Ozkan [5] have

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reported the Raman spectra of  $\text{MoO}_3$  exchanged with  $^{18}\text{O}$  tracer. Guerrero-Ruiz et al. [10] have studied the  $\text{MoO}_3$  catalyst exchanged with  $^{18}\text{O}$  using SIMS analysis. These workers discussed what oxygen species are responsible for oxidation. More studies will need to elucidate lattice oxygen species or vacancies responsible for oxidation or reoxidation, respectively, on  $\text{MoO}_3$ .

In this work, the following exchange was attempted through redox reactions:



The  $(\text{MoO}_3)^*$  exchanged partly with  $^{18}\text{O}$  tracer was recorded on a laser Raman spectrometer. The extent of Raman band shifts have been determined and compared with each other. Using the reactants of  $1\text{-C}_4\text{H}_8$  and  $^{18}\text{O}_2$ , the lattice oxygens of  $\text{MoO}_3$  were also exchanged with  $^{18}\text{O}$  through a catalytic oxidation. The results were compared with those by a reduction–oxidation method. The correlation between the Raman bands and the stretching vibration modes reported previously on  $\text{MoO}_3$  [12,13] was applied to the estimation of oxygen species and anion vacancies.

## 2. Experimental

### 2.1. Catalysts

The  $\text{MoO}_3$  supported on  $\text{SiO}_2$  (7 atom%) was prepared as follows: the desired amount of ammonium heptamolybdate were mixed in the solution. After evaporation on a water bath, it was heated at 723 K for 6 h.

### 2.2. Procedures

The first method for  $^{18}\text{O}$  substitution, i.e., a reduction–oxidation method, is as follows: the reduction of catalysts by but-1-ene was carried out in a circulation system (ca. 290  $\text{cm}^3$ ) at ca. 4 kPa and 673–723 K and the reoxidation by

$^{18}\text{O}_2$  (98%, MSD Co. Ltd.) was performed at the same temperature range at ca. 1 kPa. The amount of  $^{18}\text{O}$  exchanged was determined from the amount of products such as buta-1,3-diene. The second method for substitution is as follows: the mixture of but-1-ene at ca. 1.5 kPa and  $^{18}\text{O}_2$  at 0.5 kPa was reacted on  $\text{MoO}_3$ . The products of buta-1,3-diene, CO, and  $\text{CO}_2$  were analyzed by gas chromatography. The  $^{18}\text{O}\%$  in the products was determined by a mass spectrometer. The amounts of  $^{18}\text{O}$  exchanged in the  $\text{MoO}_3$  catalyst were assumed as those of  $^{16}\text{O}$  in the products.

The Raman spectra were recorded on a JASCO NR-1000 laser Raman spectrometer. An Ar-ion laser was tuned to the 514.5 nm line for excitation. The laser power was set at 150–200 mW. The data were stored on a computer and used for peak-shape analysis.

## 3. Results and discussion

### 3.1. Catalyst properties

The structure of  $\text{MoO}_3/\text{SiO}_2$  catalysts were determined by the X-ray diffraction method using  $\text{Cu K}\alpha$  radiation. The diffraction intensities of the  $\text{MoO}_3$  catalyst in this work were similar to those reported previously, so it is not oriented to a particular direction. The fraction of this crystallite was determined by a comparison of the X-ray peak intensities between the catalysts and mechanical mixtures. The  $\text{MoO}_3/\text{SiO}_2$  (7 atom%) catalyst contained ca. 100% of crystalline  $\text{MoO}_3$ . The results indicate that  $\text{MoO}_3$  on  $\text{SiO}_2$  is almost crystallized. The crystal sizes were determined from line broadening using several diffraction lines. The average sizes were determined as ca. 80 nm.

### 3.2. Structure of $\text{MoO}_3$ , Raman spectra of $\text{MoO}_3$ , and assignments to the normal vibrations

The structure of  $\text{MoO}_3$  was investigated by some workers [11]. It can be described as a

layer structure in which each layer is built up of  $\text{MoO}_6$  octahedra (Fig. 1a) at two levels connected in the direction to *c* axis by edge and corner sharing so as to form zig-zag rows [12,1]. In the direction to the *a* axis the octahedra are connected by corner sharing. The Mo–O distances of the distorted octahedrons are shown in Fig. 1a and b. The shortest one is 1.67 Å and is designated as terminal oxygen (I:OMo) [12,13]. In the *a* axis direction, the long Mo–O bond (2.23 Å) on  $\text{Mo}_1$  and short bond (1.73 Å) on  $\text{Mo}_2$  are connected, designated as two-connected bridged oxygens (II:OMo<sub>2</sub>). In the zig-zag rows, there is an oxygen surrounded by Mo with 1.95, 1.95 and 2.33 Å distances, which is designated as III:OMo<sub>3</sub> [12,1].

IR and Raman spectra of  $\text{MoO}_3$  were studied by some workers [12–15]. Beattie and Gilson [13] have made an attempt to apply group frequency assignments to the vibrational spectra of oxides such as  $\text{MoO}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{TiO}_2$  and etc. With  $\text{MoO}_3$ , the terminal oxygens (OMo), two-connected bridging oxygens (OMo<sub>2</sub>) and three-connected bridging oxygens (OMo<sub>3</sub>) were

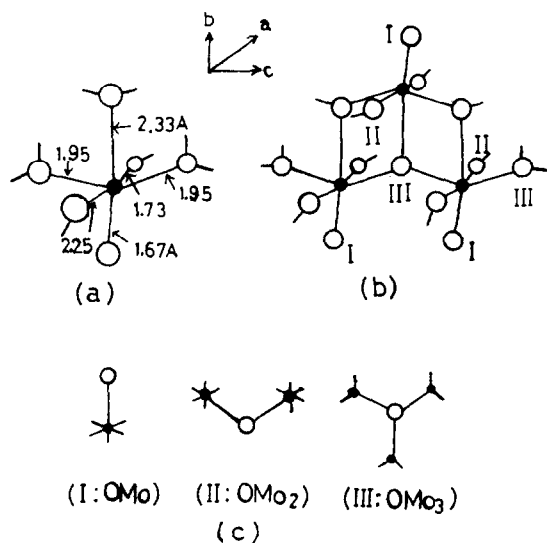


Fig. 1. Structure of  $\text{MoO}_3$  [1,12]. (a) Mo octahedron and Mo–O distances. (b) Zig-zag chains of octahedra. The oxygen types I, II, and III are shown in (c). (c) Subclassifications of bonding and bridging oxygen atoms. Filled and open circle denote Mo and oxygen, respectively.

Table 1  
IR and Raman spectra of single crystal of  $\text{MoO}_3$  reported by Nazari et al. [12]

IR ( $\text{cm}^{-1}$ )	Raman ( $\text{cm}^{-1}$ )	Assignment (stretch.)	Corresponding Mo–O bond (Å)
1007			
998		(OMo) $B_{3u}$	1.67
	993	(OMo) $A_{1g}, B_{1g}$	1.67
885		(OMo <sub>2</sub> ) $B_{3u}$	
810		(OMo <sub>2</sub> ) $B_{3u}$	1.73, 2.25
	817	(OMo <sub>2</sub> ) $B_{1g}$	1.73, 2.25
	664	(OMo <sub>3</sub> ) $B_{3g}$	1.95 (2), 2.33
566		(OMo <sub>3</sub> ) $B_{1u}$	1.95 (2), 2.33

OMo, OMo<sub>2</sub>, and OMo<sub>3</sub> are shown in Fig. 1.

considered on the basis of a site symmetry. Nazri and Julien [12] have studied the infrared and Raman polarized spectroscopy using single crystal of  $\text{MoO}_3$ . They gave the assignment of observed bands as shown in Table 1, which are the same as those by Beattie and Gilson [13]. Modes of the OMo terminal lie in the range 885 to 1007  $\text{cm}^{-1}$ . The Raman-active band at 993  $\text{cm}^{-1}$  is corresponding to the stretching mode of the Mo–O with 1.67 Å distance. The bridging oxygens (OMo<sub>2</sub>) correspond to Mo–O–Mo with the Mo–O distances of 1.73 and 2.25 Å, which is corresponding to the band at 817  $\text{cm}^{-1}$ . The vibrational mode corresponding to 664  $\text{cm}^{-1}$  is assigned to the stretching of the bridging oxygens of OMo<sub>3</sub>. Previous workers [12,13] explained that the modes of OMo<sub>3</sub> have a motion parallel to the basal ac-plane and pass perpendicularly through the 2.33 Å bond. They also explained [13] that the long 2.33 bond is being deformed while one short 1.95 bond is being compressed at the same time as the other 1.95 one is being stretched.

### 3.3. Raman band shifts of $\text{MoO}_3$ catalyst exchanged with $^{18}\text{O}$ by a reduction–oxidation method

0.03 g of  $\text{MoO}_3/\text{SiO}_2$  (7 atom%) was reduced with but-1-ene at 673–753 K. After evacuation, it was reoxidized with  $^{18}\text{O}_2$  at the same temperature. The selectivity to buta-1,3-diene

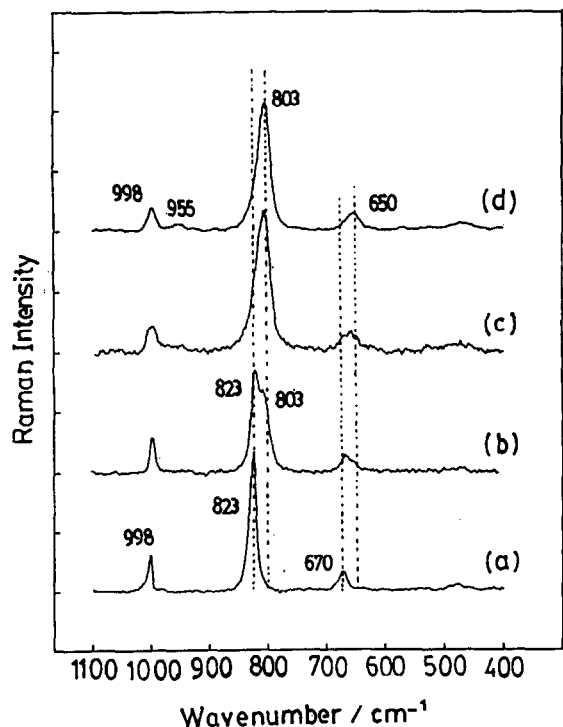


Fig. 2. Raman spectra of  $\text{MoO}_3$  exchanged with  $^{18}\text{O}$  tracer using the reduction–oxidation method. (a) No exchange. (b) 7  $\mu\text{mol}$  (7%) of  $^{18}\text{O}$  exchanged. (c) 13  $\mu\text{mol}$  (13%). (d) 23  $\mu\text{mol}$  (23%).

was above 90%. 0.03 g catalyst contains ca. 100  $\mu\text{mol}$  oxygens as  $\text{MoO}_3$ . Fig. 2 shows the spectra of  $\text{MoO}_3$  before and after they were exchanged with  $^{18}\text{O}$ . The bands at 998, 823, and 670  $\text{cm}^{-1}$  were observed (Fig. 2a) which are nearly the same as the  $\text{MoO}_3$  bands at 993, 817, and 664  $\text{cm}^{-1}$  reported by Nazari and Julien [12]. With the sample (Fig. 2b) exchanged with  $^{18}\text{O}$  by 7%, the bands at 823  $\text{cm}^{-1}$  decreases and the new band at 803  $\text{cm}^{-1}$  appears. The band at 670  $\text{cm}^{-1}$  shows line broadening. With the 13% and 23% samples, the 823  $\text{cm}^{-1}$  band is shifted to 803  $\text{cm}^{-1}$  and the 670  $\text{cm}^{-1}$  band to 650  $\text{cm}^{-1}$ . The new band at 955  $\text{cm}^{-1}$  appears, which is shifted from 998  $\text{cm}^{-1}$  (Fig. 2d). The theoretical shifts between  $\text{Mo}-^{16}\text{O}$  and  $\text{Mo}-^{18}\text{O}$  is calculated as ca. 45  $\text{cm}^{-1}$  at around 990  $\text{cm}^{-1}$  and 40–30  $\text{cm}^{-1}$  at around 800–700  $\text{cm}^{-1}$ . The shift of 43  $\text{cm}^{-1}$  for 998  $\text{cm}^{-1}$  band is the same as theoretical one. This indicates that the terminal  $\text{Mo}=\text{O}$  bond can be applicable

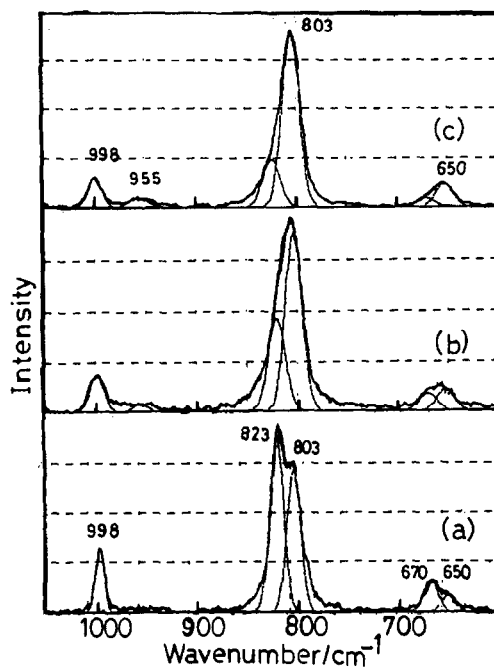


Fig. 3. The peak shape analysis of Fig. 2. (a) b in Fig. 2. (b) c in Fig. 2. (c) d in Fig. 2.

to the diatomic approximation. The bands at 823 and 670  $\text{cm}^{-1}$ , however, are shifted by only ca. 20  $\text{cm}^{-1}$ . As described above, these bands are corresponding to two-connected or three-connected bridged oxygen vibrations. This seems to suggest that the diatomic approximation is not applicable.

In order to know the shift change in details, the peak shape analysis was attempted with these spectra (Fig. 3). As shown in the figure, the good curve fittings are obtained in the cases that the 823  $\text{cm}^{-1}$  band is shifted to 803  $\text{cm}^{-1}$ , the 670  $\text{cm}^{-1}$  band to 650  $\text{cm}^{-1}$ , and the 998  $\text{cm}^{-1}$  band to 955  $\text{cm}^{-1}$ . The exchange fraction

Table 2  
Fractions of the band shifted after exchange with the  $^{18}\text{O}$  tracer for the  $\text{MoO}_3/\text{SiO}_2$  catalyst

Average % exchanged	$I_{955}/I_{998}$	$I_{803}/I_{823} +$ $I_{803}$	$I_{650}/I_{670} +$ $I_{650}$
0	0	0	0
7	0	0.45	0.35
13	0.18	0.65	0.54
23	0.30	0.78	0.71

was compared with each band between the original peak and the shifted one. The fractions are shown in Table 2. With the 7% exchanged sample, the fraction is ca. 45% for the 823  $\text{cm}^{-1}$  band and ca. 35% for the 670  $\text{cm}^{-1}$  band. With increasing in the average % exchanged with  $^{18}\text{O}$ , both bands at 823 and 670  $\text{cm}^{-1}$  were exchanged preferentially. After that, the 998  $\text{cm}^{-1}$  band was exchanged. The exchange fractions with the 823 and 670  $\text{cm}^{-1}$  bands are extremely higher than the average exchange %. This suggests that the information of Raman spectra comes from the near surface of  $\text{MoO}_3$  crystal and that surface oxygens are well exchanged.

Propene oxidation was performed previously using a  $^{18}\text{O}_2$  tracer in order to obtain information concerning the extent of lattice–oxygen participation [19]. The products such as propenal,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  were diluted with lattice oxygen ( $^{16}\text{O}$ ) in spite of the use of 98% of  $^{18}\text{O}_2$ . Using exponential dilution proposed by Keulks et al. [20], the extent of lattice–oxygen participation were determined as ca. 5 layers for  $\text{MoO}_3$  at 400°C. This indicates that the reaction takes place at a very thin surface on the  $\text{MoO}_3$  catalyst.

### 3.4. Raman band shifts of $\text{MoO}_3$ catalyst exchanged with $^{18}\text{O}$ by a catalytic oxidation using 1- $\text{C}_4\text{H}_8$ and $^{18}\text{O}_2$

Fig. 4 shows the results of catalytic oxidation using a mixture of 1- $\text{C}_4\text{H}_8$  and  $^{18}\text{O}_2$  over the  $\text{MoO}_3$  (7 atom%)/ $\text{SiO}_2$  catalyst. The amounts of products and  $^{18}\text{O}\%$  in them are shown in Table 3. The average per cent exchanged with  $^{18}\text{O}$  in the catalysts were calculated from  $^{16}\text{O}\%$  in the products assuming that the reoxidation of  $\text{MoO}_3$  takes place completely. The  $^{18}\text{O}\%$  in  $\text{H}_2\text{O}$  is assumed to be the same as that in  $\text{CO}$  and  $\text{CO}_2$ . With the Raman band at 823  $\text{cm}^{-1}$  of the catalyst whose oxygen are exchanged with 11% of  $^{18}\text{O}$ , a new shoulder appears at ca. 800  $\text{cm}^{-1}$ . With the 26% sample, this shoulder become larger and the band at 670  $\text{cm}^{-1}$  shows

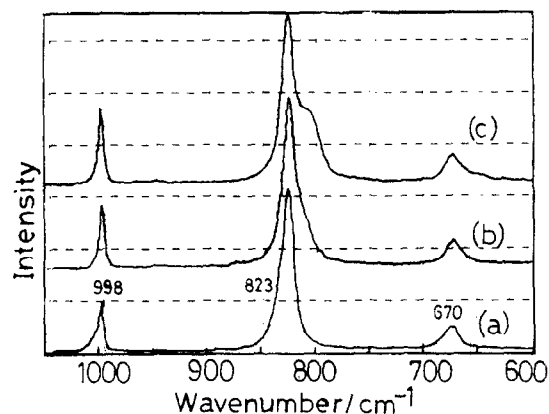


Fig. 4. Raman spectra of  $\text{MoO}_3$  exchanged with  $^{18}\text{O}$  during catalytic oxidation of but-1-ene. (a) No exchange. (b) 11% of  $^{18}\text{O}$  exchanged. (c) 26% of  $^{18}\text{O}$  exchanged. See Table 3.

line broadening. However, the new band shifted from 998  $\text{cm}^{-1}$  does not appear. In order to elucidate the shift change in details, the band changes are determined by shape analysis (Fig. 5). Table 4 lists the band intensity ratio (peak area). The ratio of  $I_{803}/(I_{823} + I_{803})$  is increasing from 13 to 34% with increasing  $n$  the average exchange % from 11 to 26%. The  $I_{650}/(I_{670} + I_{650})$  is also slightly increased from ca. 9 to 15%. These results indicate that the band at 823  $\text{cm}^{-1}$  initially exchanged with  $^{18}\text{O}$ . This tendency is the same as the results by the reduction–oxidation method described above. Furthermore, the band at 998  $\text{cm}^{-1}$  is not replaced initially by  $^{18}\text{O}$  in the case of catalytic oxidation.

Table 3

Oxidation of but-1-ene using  $^{18}\text{O}_2$  over  $\text{MoO}_3/\text{SiO}_2$ ,  $P(1-\text{C}_4\text{H}_6) = 16$  Torr,  $P(^{18}\text{O}_2, 98 \text{ atom}\%) = 4$  Torr

Temp.	Conversion %	Selectivity (%) and $^{16}\text{O}$ (%) <sup>a</sup>			Average exchange % <sup>b</sup> of catalyst
		$\text{C}_4\text{H}_6$	$\text{CO}$	$\text{CO}_2$	
473	3.3	89	6 (69)	5 (75)	11
500	6.8	82	9 (53)	9 (63)	26

<sup>a</sup> The  $^{16}\text{O}\%$  in  $\text{H}_2\text{O}$  is assumed as the average values of  $\text{CO}$  and  $\text{CO}_2$ .

<sup>b</sup> Average exchange % in the catalysts was calculated from  $^{16}\text{O}\%$  of  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ .

1 Torr = 133.3 Pa.

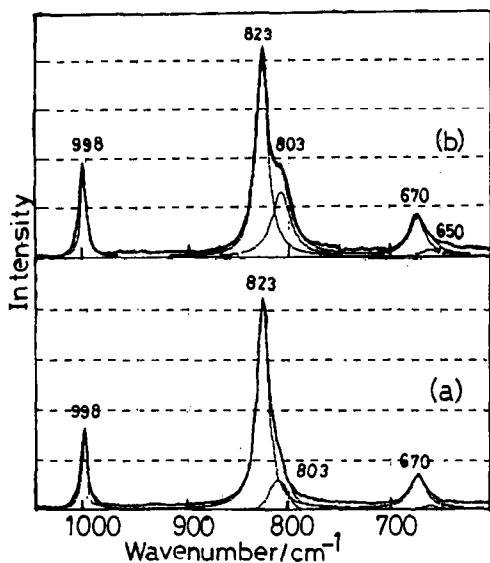


Fig. 5. The peak shape analysis of Fig. 4. (a) b in Fig. 4. (b) c in Fig. 4.

### 3.5. Active sites for reoxidation and oxidation on $\text{MoO}_3$

As discussed above, the band at  $823\text{ cm}^{-1}$  is corresponding to the stretching vibration of Mo–O for  $1.73\text{ \AA}$  and  $2.25\text{ \AA}$  in the Mo square of the octahedron (Fig. 1). This is also corresponding to the corner-linked oxygen of two octahedra to the a axis direction. The band at  $670\text{ cm}^{-1}$  is mainly corresponding to the vibration of Mo–O with two  $1.95\text{ \AA}$  distances. These oxygens are edge-linked to the c axis direction. The band at  $998\text{ cm}^{-1}$  correspond to the terminal Mo=O of  $1.67\text{ \AA}$ . The oxygens which are replaced preferentially are those of  $823$  and  $670\text{ cm}^{-1}$  bands during but-1-ene oxidation. These results suggest that the oxygens of Mo–O layer along the a or c direction have high mobilities

Table 4  
Fractions of the band shifted after exchange with the  $^{18}\text{O}$  tracer during catalytic oxidation for the  $\text{MoO}_3/\text{SiO}_2$  catalyst

Average % exchanged	$I_{955}/I_{998} +$ $I_{955}$	$I_{603}/I_{823} +$ $I_{803}$	$I_{650}/I_{670} +$ $I_{650}$
11	0	0.13	0.09
26	0	0.34	0.15

while that those of oxygen layer, i.e., (010) oxygens, have low mobilities as reported by Guerrero-Ruiz et al. [10].

If the anion vacancies move easily to other sites during reduction and oxidation catalysis, reoxidation may occur randomly at various sites, i.e.,  $^{18}\text{O}$  exchange will occur equally at various oxygen species. However, the preferential exchange takes place as described above. These results suggest that the reoxidation by  $^{18}\text{O}_2$  at the surface may take place mainly at the anion vacancies corresponding to the Mo–O of  $1.73\text{ \AA}$  ( $\text{OMo}_2$ ) and of  $1.95\text{ \AA}$  ( $\text{OMo}_3$ ).

The reduction of  $\text{MoO}_3$  and its XPS study was performed by some workers. Grunert et al. [16] have reported that the  $\text{Mo}^{6+}$ ,  $\text{Mo}^{5+}$ , two different  $\text{Mo}^{4+}$ , and  $\text{Mo}^{2+}$  will be present in the  $\text{MoO}_3$  from which lattice oxygens are released at high temperatures. Haber et al. [17] have proposed the presence of  $\text{Mo}^{6+}$  and two different  $\text{Mo}^{4+}$  after the reduction of  $\text{MoO}_3$ . Broclawik et al. [18] have suggested that the oxidation number of Mo is lowered from  $6+$  to  $4+$  without change of crystal structure in the first stage of reduction while the structure changes in the stage of more reduction from corner-linked octahedra to edge-sharing octahedra using SCF-SW-Xa calculations for Mo–O oxide anions. The oxygen insertion means the reoxidation of  $\text{Mo}^{5+}$  and  $\text{Mo}^{4+}$  to  $\text{Mo}^{6+}$ . In this case, oxygen insertion seems to take place on vacancies or by returning edge-sharing octahedra to corner-sharing octahedra.

Volta et al. [1] have reported that the (100) plane is responsible for mild oxidation and the (010) plane for total oxidation in propene oxidations. Abon et al. [2] have recently reported that the (120) plane is also responsible for propenal formation in propene oxidation. On the other hand, Jiolkowski [3] has observed that the (010) plane is inactive but the (001) is active for propenal formation. Bruckman et al. [4] have reported that the reactivity of allyl iodide runs parallel with the fraction of (010) planes where propenal formation occurs.

The  $\text{MoO}_3$  catalyst used in this work was not

oriented to a special direction. The oxidative dehydrogenation of but-1-ene seems to take place on any surface oxygens of these planes since the allyl hydrogen is abstracted more easily from it. It is unclear which plane is more active for the reaction in this work. The  $\text{OMo}_2$  oxygens (1.73 Å) are present on the (100) plane. The  $\text{OMo}$  ones (1.67 Å) are present on the (010) plane. It is unlikely that the (010) oxygens are more active than other species, since they did not exchanged and did not diffuse so rapidly during oxidation reactions.

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