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Structure and reactivity of MoO_3-MgO catalysts

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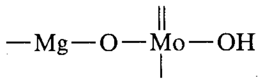
Surface of OH groups on reduced MoO_2-MgO catalysts such as



$$-Mg-O-\overset{\|}{\underset{|}{Mo}}-OH$$

may act as an active site for hydrogenation of propene. The surface hexa-coordinated Mo^{5+} ion (Mo^{5+}_{6c}) was reduced to a lower number of cation such as Mo^{4+} or Mo^{3+} which act as an active site for metathesis of propene.

Keywords: Metathesis; hydrogenation; molybdenum oxide; magnesium oxide; EXAFS; ESR

1. Introduction

The structure and reactivity of supported molybdenum oxide catalysts are currently subject of many investigations. Some binary metal oxides containing MoO_3 are used as catalysts for the isomerization, oxidation, hydrogenation and metathesis of olefin [1,2]. It is well known that the surface OH group on MoO_3 catalysts acts as an acid site [3], and surface Mo^{6+} is easily changed to Mo^{5+} and/or Mo^{4+} with the reduction [4–7]. MoO_3 supported on ZrO_2 shows the highest catalytic activity for the reduction of NO with H_2 at 557 K. While, MoO_3 supported on MgO shows one of the lowest catalytic activity [8]. We previously reported that the non-basic surface OH groups determined by the reaction between DPPH (2,2-diphenyl-1-picrylhydrazil) and the surface of MoO_3-TiO_2 acts as active sites for isomerization of 1-butene [9]. Thus, the general formation of an active site on binary catalysts containing MoO_3 could not clearly be discussed.

In the present investigation, the formation of active sites for metathesis and hydrogenation of propene are discussed from the results of the surface structure and reactivities on oxidized or reduced MoO_3-MgO catalysts. The structures are determined by XAFS, XRD and ESR.

2. Experimental

2.1. PREPARATION OF SAMPLES

Oxidized MoO_3-MgO catalysts (atomic ratio of Mo/Mg from 0.1 to 0.9) were prepared by the impregnation technique. Calculated amounts of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ were dissolved in a volume of H_2O corresponding to the $MgCl_2 \cdot 6H_2O$ to be impregnated at the temperature of 363 K. The impregnate was air-dried for 10 h at 383 K, and finally heat-treated at 873 K for 1 h in air.

Reduced catalysts were prepared in atmospheric H_2 flow at 773 K for 1 h.

Fig. 1 shows the electroconductivities of oxidized and reduced MoO_3-MgO. The same values of $-\log \sigma$ were observed on oxidized catalysts any containing MoO_3. However, on the reduced catalysts containing MoO_3 above 0.5 atomic ratio of Mo/Mg, the values of $-\log \sigma$ were decreased. The facts suggest that increase of electroconductivity is mainly caused by the reduction of surface Mo ions.

2.2. REACTION BETWEEN DPPH AND THE SURFACE

A weighed MoO_2-MgO sample (10 mg) and 0.5 ml of 1×10^{-3} mol/l DPPH (2,2-diphenyl-1-picrylhydrazil) benzene solution was introduced into a 4 mm i.d. ESR sample tube and reacted at 293 K. The reaction between the surface species and DPPH reached its equilibrium after 48 h. The total number of surface species was calculated based on decreased concentration of DPPH radical measured by ESR. The number of hydrogen radical donor sites on the surface of catalysts was calculated from the concentration of $DPPH_2$ (1,1-diphenyl-2-picrylhydrazine) formed by the reaction. The concentration of formed $DPPH_2$ can be calculated from the shift of the UV spectrum from 330 nm ($>$N–$\underset{\cdot}{\mathrm{N}}$–) to 317 nm ($>$N–NH–) and the concentration of the remaining DPPH radical.

2.3. METATHESIS AND/OR HYDROGENATION OF PROPENE

The reactions were carried out in a conventional circulation system, the catalysts were pretreated at 773 K in vacuo before the reaction. The reaction conditions were as followed: the temperature of the reaction: 423 K; the pressure of propane: 150 Torr; the hydrogen pressure in the case of hydrogenation: 150 Torr, the amount of catalysts: 100 mg. The products were analyzed by gas chromatography.

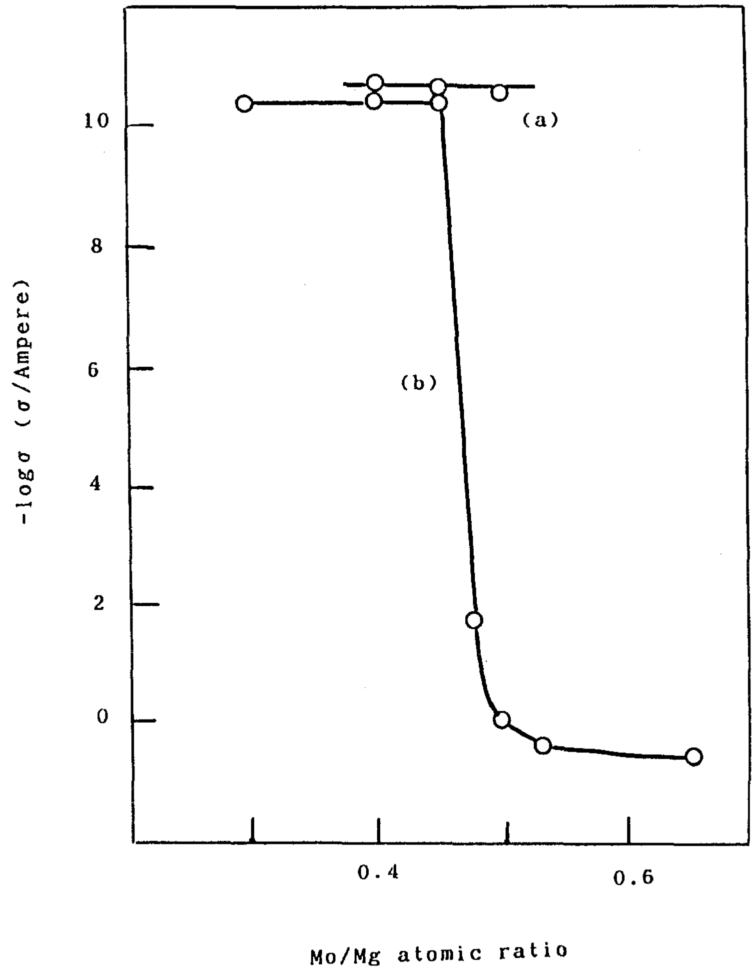


Fig. 1. Change of electroconductivities, $-\log \sigma$, on (a) oxidized and (b) reduced MoO_3-MgO catalysts.

2.4. MEASUREMENTS OF Mg K-EDGE AND Mo K-EDGE XAFS

Mg K-edge absorption XAFS spectra were measured at BL 7B of UVSOR of the institute of Molecular Science and Mo K-edge absorption XAFS at 10C of the Photon Factory (PF) of the National Laboratory for High Energy Physics.

2.5. MEASUREMENTS OF ESR SIGNALS

X-band ESR signals were recorded on a JEOL JES-3ME spectrometer at room temperature. g-values were determined by using Mn^{2+} marker as a reference.

3. Results and discussion

3.1. STRUCTURE OF CATALYSTS

3.1.1. *XRD results*

From XRD results as shown in fig. 2, the formation of $MgMoO_4$ is observed in the sample of oxidized MoO_3-MgO catalysts containing above 0.5 atomic ratio of Mo/Mg, while MoO_3 structure was formed in the catalysts containing above 0.6 atomic ratio.

3.1.2. *Mg and Mo K-edge XAFS studies*

In any reduced MoO_3-MgO (Mo/Mg = 0.1–0.9) catalysts, clear Mg K-edge XANES spectra could not observed.

Mg K-edge XANES pattern of oxidized catalysts as in fig. 3, the line intensity at 1305 eV due to the white line of Mg K-edge was decreased with increasing

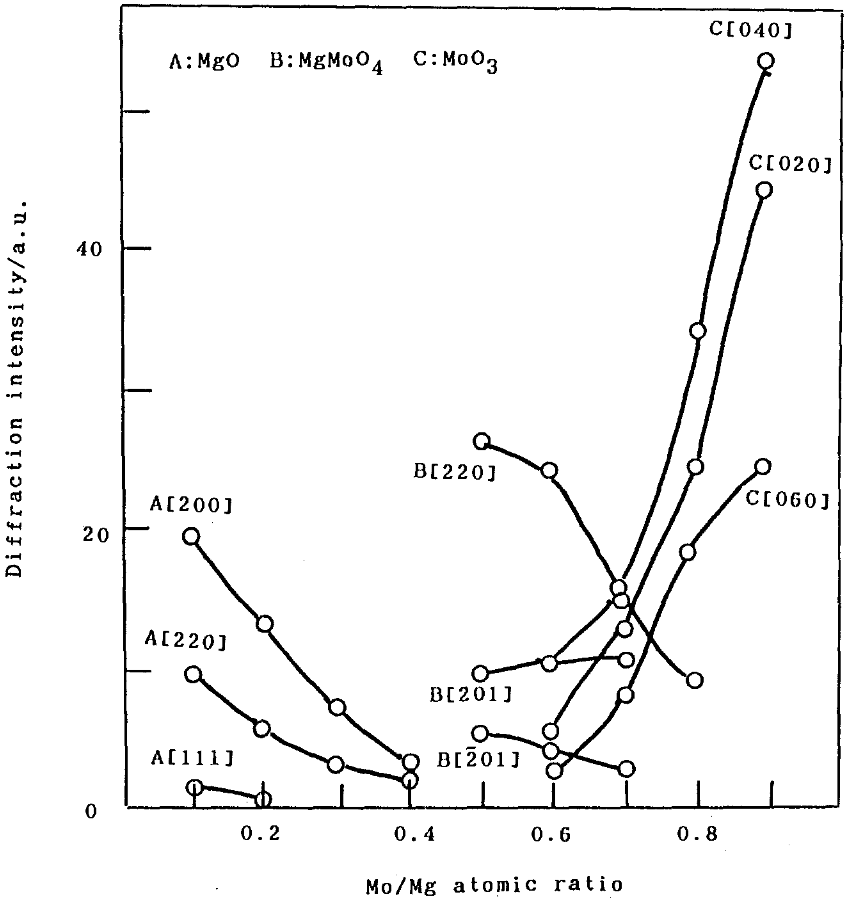


Fig. 2. X-ray diffraction intensity on oxidized MoO_3-MgO.

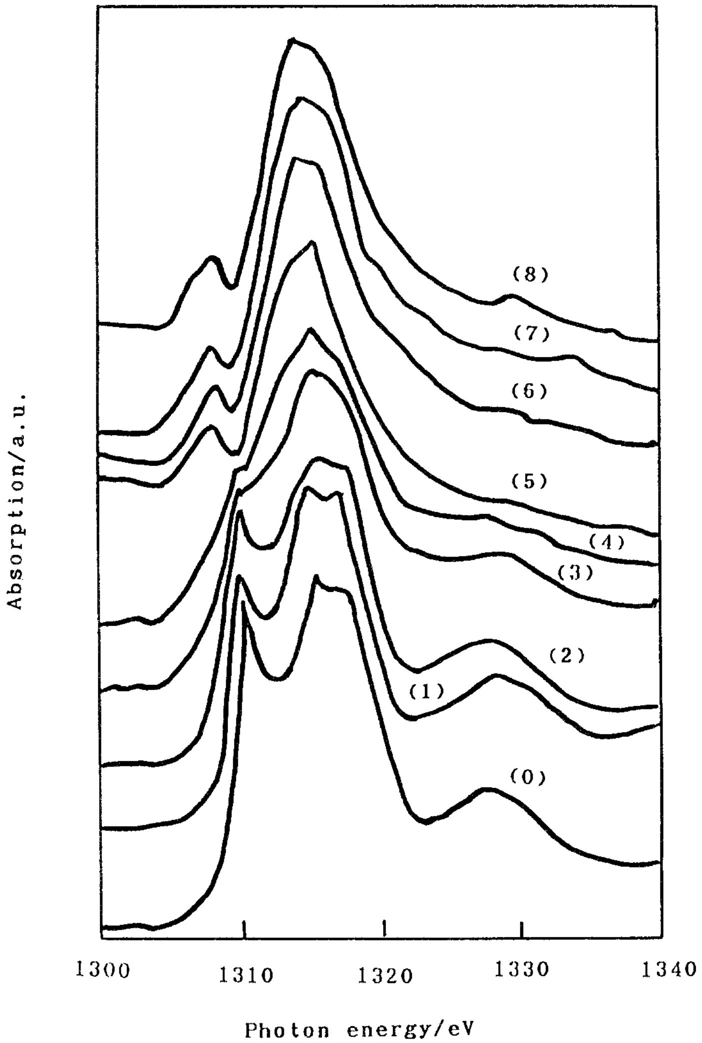


Fig. 3. Mg K-edge XANES pattern of (1–8)oxidized MoO_3-MgO and (0)MgO. Mo/Mg atomic ratio: (1)0.1, (2)0.2, (3)0.3, (4)0.4, (5)0.5, (6)0.6, (7)0.7, and (8)0.8.

the Mo contents in MgO. The distances from Mg ion to the O ion (the first ligand: L1) and to the next Mg ion or Mo ion (the second ligand: L2) are calculated from Fourier transformed EXAFS data of k^3-weight of Mg K-edge in MoO_3-MgO catalysts. The values of L1/L2 ratio are increased on the sample of Mo containing over 0.5 in MgO as shown in fig. 4. In the case of Mo contents under 0.4, the pattern of XANES and Fourier transform of Mg K-edge EXAFS are similar of non-doped MgO. In the case of low contents of Mo ions, the facts suggest that Mo ion existed in the bulk of MgO crystal.

Mo K-edge XANES pattern of oxidized MoO_3-MgO catalysts correspond with metal molybdate such as $CaMoO_4$ or $CaMoO_4$. On reduced MoO_3-MgO

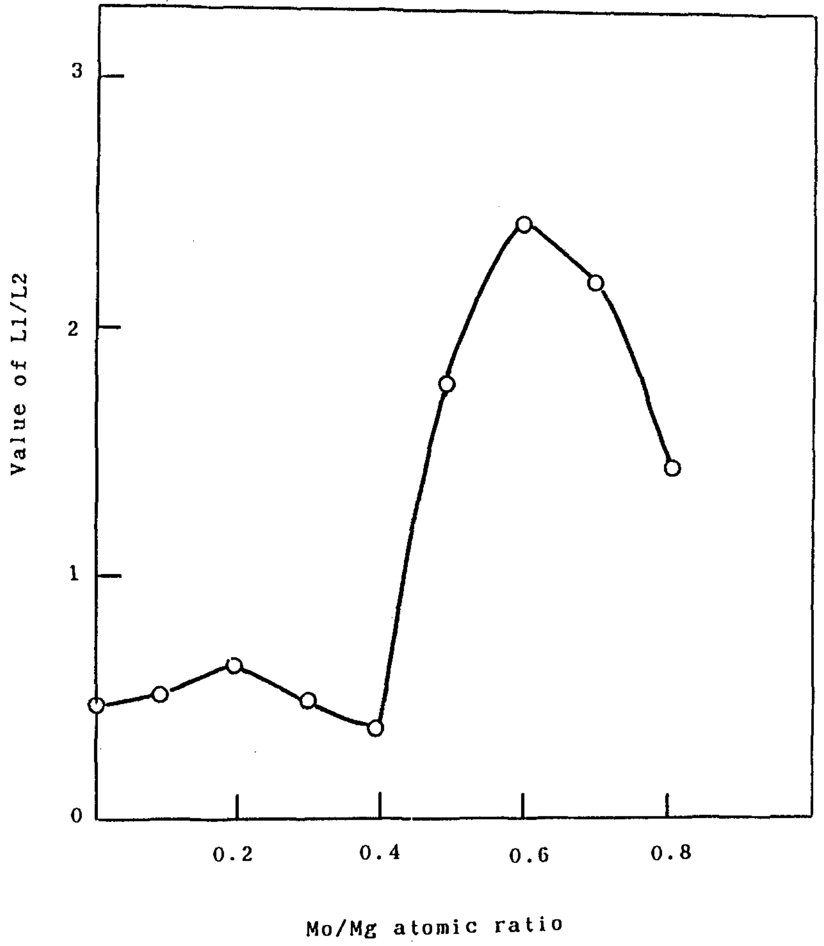


Fig. 4.Existence value of L_1/L_2 obtained by Fourier transform from Mg K-edge EXAFS of oxidized MoO_3-MgO. L_1 and L_2 indicate the distance from the Mg atom to the first and second ligand.

catalysts, XANES pattern agree with reduced MoO_3. Fourier transformed EXAFS data of k^3-weight of Mo K-edge in MoO_3-MgO catalysts is shown in fig. 5. With the reduction, the line at 2.3 Å maybe due to Mo-O-Mg has appeared. These results suggest that $MgMoO_4$ is even formed in a part of oxidized catalysts for which the atomic ratio of Mo/Mg is less than 0.6.

3.2. ESR BEHAVIOR IN MoO_3-MgO CATALYSTS

As shown in fig. 6, ESR signals due to Mo^{5+} measured at 120 K were observed in oxidized MoO_3-MgO. The various coordinative Mo^{5+} species such as Mo^{5+}_{6c}, Mo^{5+}_{5c} and Mo^{6+}_{4c} were produced in oxidized catalysts analogous the results on MoO_3-SiO_2 [10]. The maximum ESR signal intensities due to hexa-co-

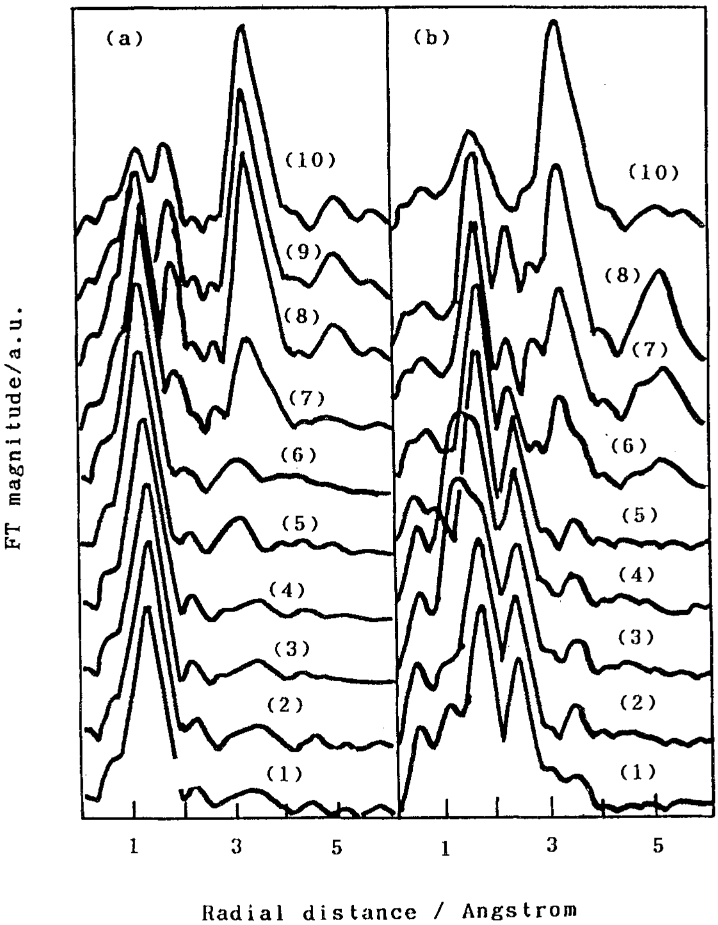


Fig. 5. Fourier transform of Mo K-edge EXAFS of (a:1–9) oxidized and (b:1–8) reduced MoO_3-MgO and (a, b:10)MoO_3. Mo/Mg atomic ratio: (1)0.1, (2)0.2, (3)0.3, (4)0.4, (5)0.5, (6)0.6, (7)0.7, (8)0.8, and (9)0.9.

ordinated Mo^{5+} ion (Mo^{5+}_{6c}) are observed in the catalysts containing from 0.5 to 0.7 atomic ratio of Mo/Mg as in fig. 7. The maximum intensity due to total Mo^{5+} was obtained in the sample of lower contents of Mo ion (atomic ratio of Mo/Mg is 0.2).

3.3. SURFACE ACTIVE SITES PROVED WITH DPPH

The numbers of hydrogen radical donor sites (HRD) were calculated from the concentration of $DPPH_2$ formed by the reaction. The reaction DPPH and HRD is schematically shown as follows:

$$\mathrm{DPPH} + \mathrm{HRD} \rightarrow \mathrm{DPPH}_2 + (\mathrm{HRD} - \mathrm{H}).$$

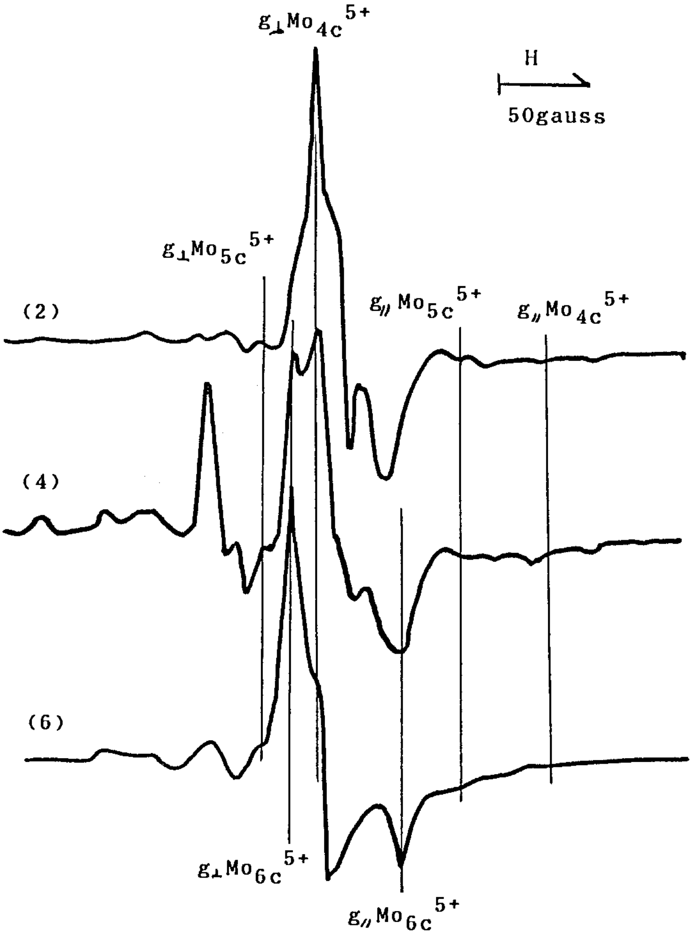
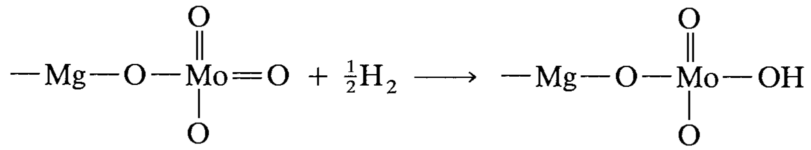


Fig. 6. ESR signals in oxidized MoO_3-MgO measured at 120 K. Mo/Mg atomic ratio: (2)0.2, (4)0.4, (6)0.6.

As shown in fig. 8, no change of the number of HRD is observed in the oxidized catalysts. In the case of reduced catalysts, maximum numbers of HRD were observed in the catalysts containing Mo at 0.6 atomic ratio of Mo/Mg. On the catalysts containing much Mo ion, Mo ion has appeared on the surface of catalysts. So, an observed HRD may be due to surface OH groups formed by reduction of catalysts such as MoO_3-TiO_2 catalysts [9]:



$$-\text{Mg}-\text{O}-\underset{\text{O}}{\underset{|}{\overset{\text{O}}{\overset{\|}{\text{Mo}}}}}=\text{O} + \tfrac{1}{2}\text{H}_2 \longrightarrow -\text{Mg}-\text{O}-\underset{\text{O}}{\underset{|}{\overset{\text{O}}{\overset{\|}{\text{Mo}}}}}-\text{OH}$$

From the results of XAFS, –Mg–O–Mo– bond is observed in the catalysts containing less Mo ion, however, the surface Mo ion disappeared.

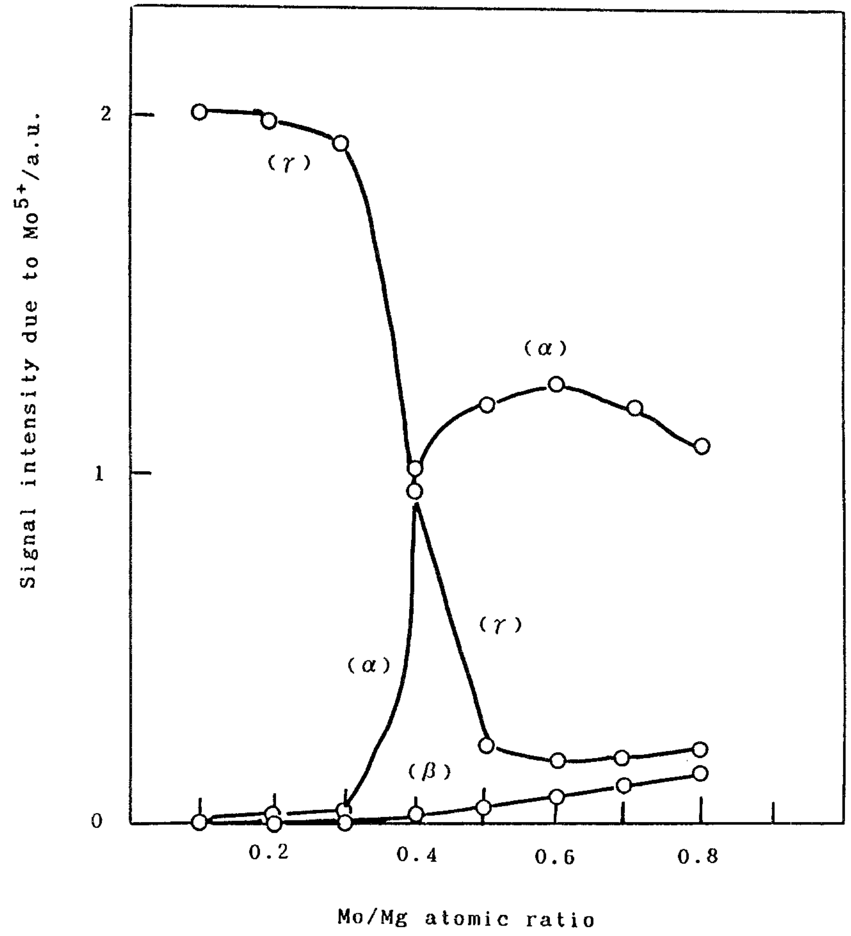
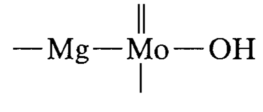


Fig. 7. Signal intensities of various coordinative Mo^{5+} species such as (α): Mo$^{5+}_{6c}$, (β): Mo$^{5+}_{5c}$ and (γ): Mo$^{6+}_{4c}$.

3.4. REACTIVITIES FOR METATHESIS OR HYDROGENATION OF PROPENE

The activities for the metathesis of propene are observed on the reduced catalysts of MoO_3 contents over 0.5 atomic ratio of Mo/Mg as shown in fig. 9. In the absence of H_2, the maximum conversion of formed ethylene, trans-2-butene, cis-2-butene and 1-butene by the metathesis of propene are 9.0, 4.0, 2.0 and 0.5%, respectively. A same conversion for each metathesis product was obtained in the presence of H_2 (150 Torr) without the formation of propane and butane. An active site for hydrogenation possibly exists independently with an active site for metathesis on the surface of reduced catalysts. Following the above section and this section, the surface OH groups such as



$$—Mg—\overset{\|}{\underset{|}{Mo}}—OH$$

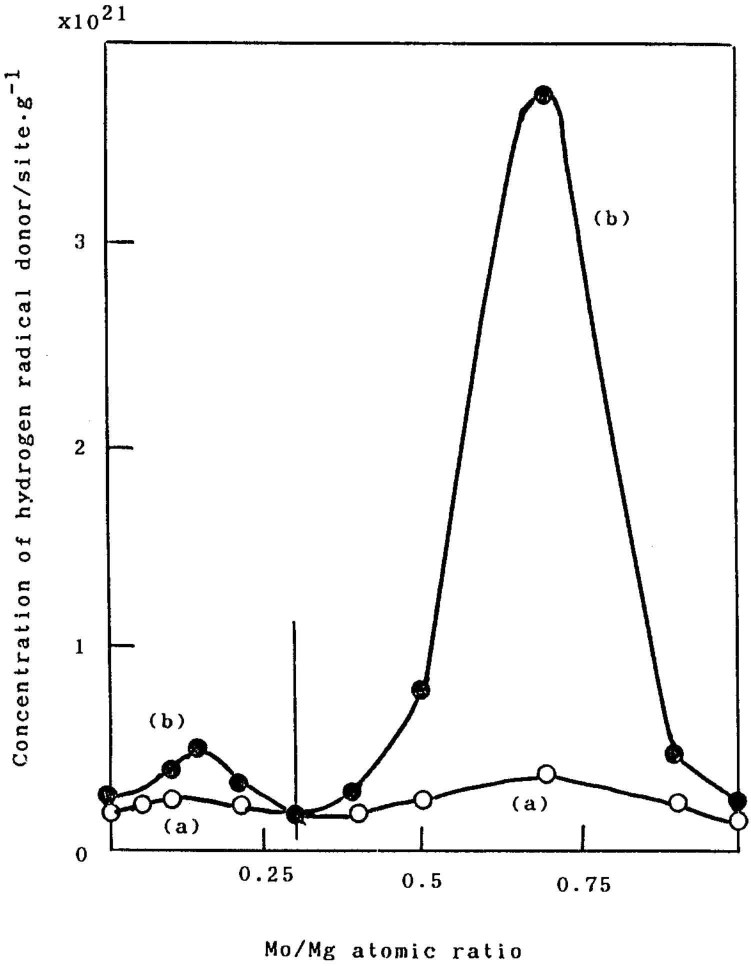


Fig. 8. The concentration of hydrogen radical donor sites on (a) reduced and (b) oxidized MoO_3-MgO.

may act as an active site for hydrogenation and the surface hexacoordinated Mo^{5+} ion (Mo_{6c}^{5+}) acts as an active site for metathesis.

4. Conclusion

The present paper reports the surface structure and reactivity for metathesis and hydrogenation of propene on oxidized and reduced MoO_3-MgO. The results are summarized as follows:

1. The changes of electroconductivities indicated that the surface reduction occurred in the case of highly containing catalysts of Mo ion.

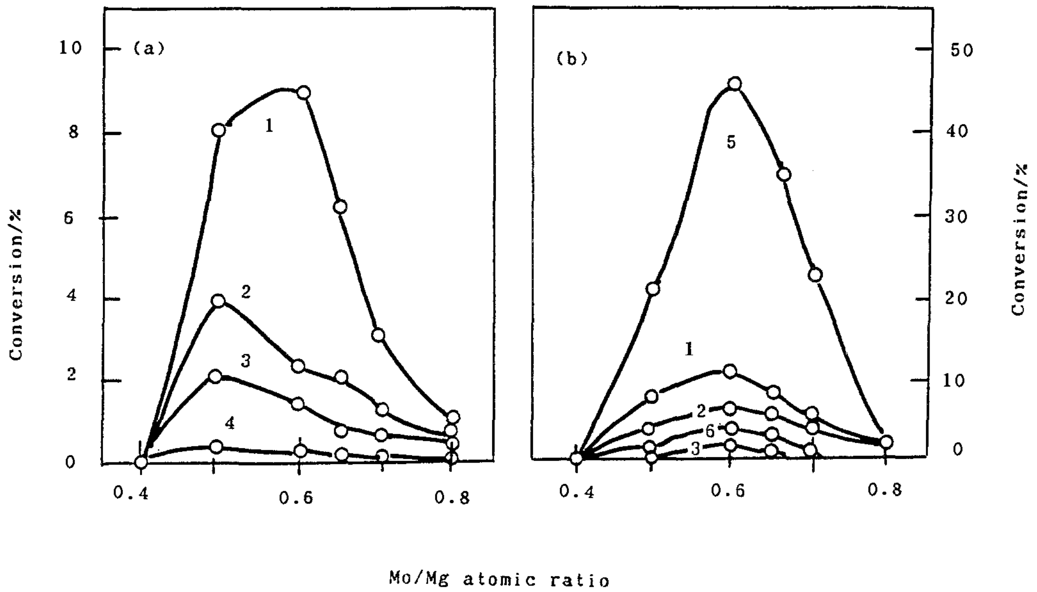
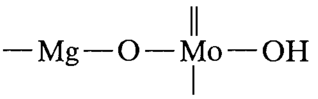


Fig. 9. Conversion of formed products by metathesis or hydrogenation of propene in the absence, (a), and in the existence, (b), of H_2. The products (1), (2), (3), (4), (5) and (6) are shown ethylene, trans-2-butene, cis-2-butene, 1-butene, propane, and n-butane, respectively.

2. The surface OH groups formed by reduction of oxidized catalysts such as



$$\text{—Mg—O—}\overset{\|}{\underset{|}{\text{Mo}}}\text{—OH}$$

may act as an active site for hydrogenation of propene.

3. The surface hexa-coordinated Mo^{5+} ion (Mo^{5+}_{6c}) was reduced to lower coordinated Mo^{5+} ion which acts as an active site for metathesis of propene.

Acknowledgments

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References

[1] J. Goldwasser, J. Engelhardt and W.K. Hall, J. Catal. 70 (1981) 275.
[2] M.B. Ward, M.J. Lin and J.H. Lunsford, J. Catal. 50 (1977) 306.
[3] N. Giordano, A. Vaghi, J.C.J. Bart and A. Castellan, J. Catal. 38 (1975) 11.

[4] J. Buiten, J. Catal. 10 (1968) 188.
[5] S.Y. Tan, Moro-oka and A. Ozaki, J. Catal. 17 (1970) 125.
[6] M. Ai and T. Ikawa, J. Catal. 40 (1975) 203.
[7] Ph.A. Batist, A.H.W.M. Der Kinderen, Y. Leeuwenburgh, F.A.M.G. Metz and G.C.A. Schuit, J. Catal. 12 (1968) 45.
[8] K. Tanabe, H. Ikeda, T. Iizuka and H. Hattori, React. Kinet. Catal. Lett. 11 (1979) 149.
[9] S. Hasegawa, M. Kudo and T. Tanaka, in: *Acid-Base Catalysis*, eds. K. Tanabe et al. (Kodansya-VCH, 1989) p. 183.
[10] C. Louis and M. Che, J. Phys. Chem. 91 (1987) 2875.