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Carrier Effect in Vapor-Phase Oxidation of Butadiene Over Supported Molybdena Catalysts

MASAMICHI AKIMOTO AND ETSURO ECHIGOYA

Department of Chemical Engineering, Tokyo Institute of Technology
Ookayama, Meguro-ku, Tokyo, Japan

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The reactivity of Mo^{5+} with adsorbed oxygen formed on various kinds of supported molybdena catalysts has been investigated by ESR. The results are discussed as a carrier effect with reference to the selectivity for maleic anhydride formation during vapor-phase oxidation of butadiene. Mo^{5+} formed on silica and titania carrier can be easily oxidized and shows good selectivity, in contrast to Mo^{5+} on magnesia and alumina. By ESR, there appeared only one adsorbed oxygen species O_2^- on MoO_3–MgO, MoO_3–Al_2O_3 and MoO_3–SiO_2, while two kinds of adsorbed oxygen species, O_2^- and O^-, were observed on MoO_3–TiO_2.

It was also shown that O_2^- and O^{2-}, which was formed by the oxidation of Mo^{5+} and proved to be $Mo^{6+}{=}O^{2-}$, were required for the production of maleic anhydride. Therefore, it was concluded that the higher selectivity of MoO_3–SiO_2 and MoO_3–TiO_2 catalyst compared with MoO_3–MgO and MoO_3–Al_2O_3 can be attributed to the presence of the double bond oxygen.

INTRODUCTION

It has long been recognized in heterogeneous catalysis that the efficiency of a catalyst can be markedly enhanced by supporting it on a solid having large surface area. But, even now, the role of the carrier is not fully understood. There are some observations which imply a chemical interaction between active component and carrier which may play an important role in producing a carrier effect (*1–3*). These prompted us to investigate the carrier effect in the vapor-phase oxidation of butadiene over supported molybdena catalyst. In this paper, titania, silica, alumina and magnesia were used as carrier for molybdena catalyst, and the physical and chemical properties of these catalysts were studied by X-ray analysis, ESR and ir spectroscopy with reference to active sites and adsorbed oxygen species. Oxygen species, which are selective for the production of maleic anhydride, were also investigated.

EXPERIMENTAL

Catalytic oxidation of butadiene was carried out using a conventional flow microreactor at a pressure of one atmosphere. The reactor consisted of a 13 mm o.d. pyrex tube, 300 mm long with a concentric thermowell. The catalyst was diluted with quartz of the same size and Raschig rings (2.5 × 2.5 mm) were added above and below the catalyst bed. As reaction materials, air and very pure butadiene were used in all experiments. Air was purified by passing through silica-gel and a soda-lime tower.

Catalysts were prepared by mixing either alumina sol, silica sol, titania gel or magnesium hydroxide with an aqueous solution of ammonium molybdate, evaporating the mixture to dryness on a water bath and sieving the dried mass obtained into 16–32 mesh particles. The catalysts were then calcined in an air current at 540°C for 4 hr. As a source of P_2O_5, As_2O_3, Sb_2O_3, and

Bi_2O_3, 85 wt % H_3PO_4, extra pure As_2O_3, Sb_2O_3 and $Bi(NO_3)_3 \cdot 5H_2O$ were used.

The gaseous effluent from the reactor was analyzed by gas chromatography. Maleic anhydride formed was absorbed into water followed by boiling the solution to remove dissolved carbon dioxide and titration with an aqueous solution of sodium hydroxide. The structure of the catalyst was investigated by X-ray diffraction using nickel-filtered Cu *Kα* radiation. The surface area of the catalyst was determined by the BET method using nitrogen as adsorbate. The amount of Mo^{5+} formed in the catalyst was measured by ESR with Mn^{2+} as an internal standard. The effect of temperature on the amount of adsorbed oxygen species was also studied by the above-described method, but in this case the catalyst (50 mg) was evacuated at 540°C for 1 hr and at about −100°C, oxygen was introduced at a pressure of 5 mm Hg. A temperature-programmed cavity was used for the ESR studies.

RESULTS AND DISCUSSION

Active Site in the Oxidation of Butadiene over Supported Molybdena Catalysts

Silica, alumina, and magnesia showed very low activity in the oxidation of butadiene, in contrast to titania. Moreover, these carriers promoted only complete combustion of butadiene, without formation of maleic anhydride. Figure 1 shows the result of the oxidation over MoO_3–TiO_2. When a small amount of molybdena was added to titania, the catalytic activity decreased, and the further addition of molybdena resulted in enhancement of the activity to reach a maximum value at a molybdena content of 25 mole %. From this result, the active site inherent to titania seems to disappear by the addition of a small amount of molybdena and then be followed by the formation of a new active site through interaction of molybdena with titania. This is also supported by the change in surface area of the catalyst. Examination of MoO_3–TiO_2 by X-ray diffraction revealed that this catalyst consists of anatase-type solid solution and that molybdena can dissolve in the titania to the extent of 25–30 mole %. Hence, a new active site was possibly formed by the dissolution of molybdena into the titania.

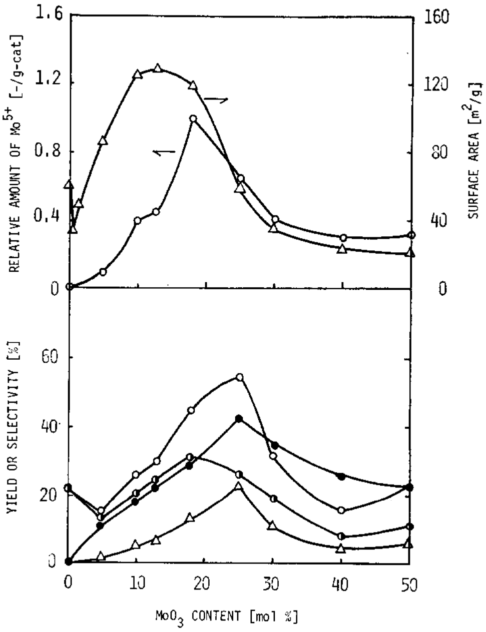

FIG. 1. Correlation between relative amount of Mo^{5+} and activity of MoO_3–TiO_2 catalyst. Reaction temp.: 380°C, butadiene concentration: 1.5 vol % in air, contact time: W/F = 0.51 [g cat hr/g mole]. ○: conversion of butadiene, ◑: yield of (CO_2 + CO), △: yield of maleic anhydride, ●: selectivity to maleic anhydride.

On the analogy of the V_2O_5–MoO_3 catalyst used in vapor-phase oxidation of benzene (*4*, *5*), a valence shift of Ti^{4+} or Mo^{6+} was expected on formation of the solid solution. Hence, MoO_3–TiO_2 was evacuated at 365°C for 30 min at 10^{-5} mm Hg and then investigated by ESR at room temperature. The presence of Mo^{5+} (g = 1.93) was observed, which was similar to the case of used catalyst and this observation is justifiable as molybdena is more easily reduced than titania. The relative amount of Mo^{5+} formed on the catalyst surface by the evacuation, i.e., the relative value of the product of Mo^{5+} concentration formed per gram catalyst by its surface area, is also shown in Fig. 1. The catalytic activity is found to be enhanced with in-

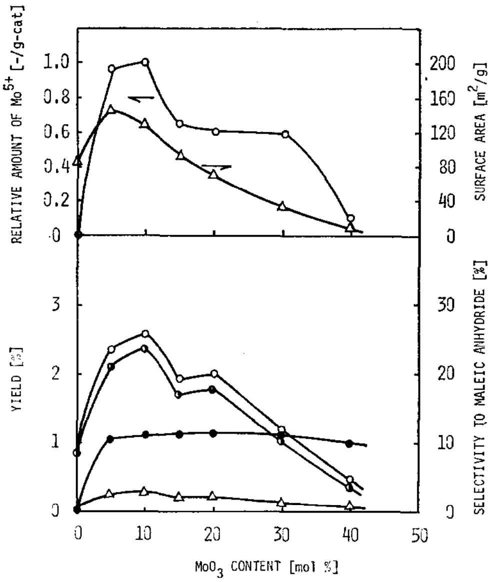

FIG. 2. Correlation between relative amount of Mo^{5+} and activity of MoO_3–MgO catalyst. Reaction temp.: 380°C, butadiene concentration: 1.5 vol % in air, contact time: $W/F = 0.51$ [g cat hr/g mole]. ○: conversion of butadiene, ◑: yield of (CO_2 + CO), △: yield of maleic anhydride, ●: selectivity to maleic anhydride.

crease in the amount of Mo^{5+} formed on the catalyst surface.

Figure 2 shows the result in the case of MoO_3–MgO catalyst, which consists of periclase-type solid solution within the molybdena content of about 40 mole %.

X-ray analysis revealed that MoO_3–Al_2O_3 catalyst is amorphous in the range of molybdena content up to 66 mole % and that the solubility of molybdena in amorphous silica is very low (<5 mole %). The selectivities were 10–12% (MoO_3–Al_2O_3) and 40–42% (MoO_3–SiO_2). In contrast to MoO_3–Al_2O_3, MoO_3–SiO_2 showed a result similar to MoO_3–TiO_2 and MoO_3–MgO in that the catalytic activity was proportional to the amount of Mo^{5+} formed on the surface. Therefore, Mo^{5+} appears to be an active site in the oxidation of butadiene.

Based on the selectivity to maleic anhydride, these carriers can be broadly divided into (A) MgO, Al_2O_3, selectivity 10–12% and (B) SiO_2, TiO_2, selectivity 40–42%. As strong acids are formed on the surface of these catalysts during the preparation, it is possible that their presence may affect the selectivity of this reaction. Thus, strong solid acids ($pK_a \leq -3.0$) were observed on alumina and their amount increased by the addition of molybdena. MoO_3–Al_2O_3 catalyst was accordingly poisoned with pyridine during the oxidation. Poisoning of the catalyst resulted in decrease of the activity and conversion of butadiene, but the selectivity remained unchanged. The other catalysts also showed the same result. Hence, it can be concluded that at the steady state, the selectivity is independent of the initial presence of strong solid acids but may be attributed to the nature of Mo^{5+} formed on the catalyst surface.

Reactivity of Mo^{5+} *with Oxygen*

Reactivity of Mo^{5+} with oxygen was investigated using ESR. A small amount of the catalyst (0.10 g) was weighed into a quartz tube and evacuated at 365°C for 30 min at 10^{-5} mm Hg. The amount of formed Mo^{5+} was determined at room temperature and then reacted with oxygen (20 mm Hg) for 30 min followed by evacuation at room temperature. The decreased amount of Mo^{5+} as a result of the oxidation was similarly determined by ESR. Figure 3 shows the reactivity of Mo^{5+} with oxygen formed in the various catalysts. It is interesting to note that unlike the Mo^{5+}(B) in MoO_3–SiO_2 catalyst, the Mo^{5+}(A) in MoO_3–MgO and MoO_3–Al_2O_3 cannot be oxidized even at 450°C. Thus, there appear two kinds of Mo^{5+}, Mo^{5+}(A) and Mo^{5+}(B), in MoO_3–TiO_2 catalyst. Mo^{5+}(A) is probably formed by a solid-phase reaction when the catalyst was prepared: Mo^{5+}(B), on the other hand, presumably formed at the sites where lattice oxygen is lost by the evacuation, appears to be easily oxidized.

Butadiene may be able to adsorb on these Mo^{5+} centers with formation of a coordination bond and the nature of these adsorbed butadiene species seems not to be so different as to affect the selectivity remarkably. Therefore, the higher activity and selectivity of Mo^{5+}(B) compared to

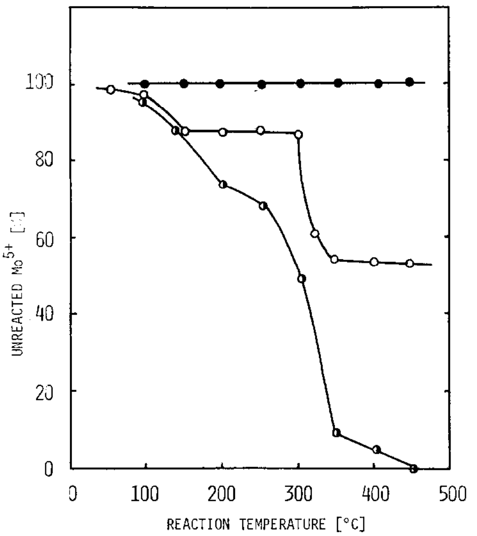

FIG. 3. Reactivity of oxygen with Mo^{5+} formed in the catalysts. ○: MoO_3-TiO_2 (1:3), ◑: MoO_3-SiO_2 (1:9), ●: MoO_3-Al_2O_3 (2:9), MoO_3-MgO (1:9).

Mo^{5+}(A) is due to the different nature of formed oxygen species rather than to that of adsorbed butadiene species. The carrier effect on the nature of Mo^{5+} will be fully studied later.

Selective Oxygen Species for Maleic Anhydride Formation

Adsorbed oxygen species formed on these catalysts have been investigated by means of ESR. The oxygen species required for the production of the anhydride, have also been predicted. There have been many papers (*6*) on the ESR spectra of oxygen species adsorbed on metal oxides. Shvets *et al.* (*7*) investigated the spectrum of oxygen species adsorbed on reduced molybdena and identified the triplet signal with g = 2.018, 2.010 and 2.004 with O_2^-. Ishii *et al.* (*8*) studied the spectrum on MoO_3–Al_2O_3 catalyst and ascribed the triplet signal with g = 2.04, 2.01, 2.00 to O_2^- and a sharp singlet signal with g = 2.00 to O^-. In our experiments, there appeared no ESR signal of adsorbed oxygen species on alumina and silica even at −100°C but the signal was observed on supported molybdena catalysts. Figure 4 shows the ESR spectrum of adsorbed oxygen species on MoO_3–TiO_2 (1:99) catalyst. At room temperature, a triplet signal with g = 2.019, 2.009, and 2.003 was observed. At 60–100°C, the signal intensity with g = 2.019 and 2.009 decreased and at the same time the signal with g = 2.002 became sharp and increased. When N_2O was adsorbed on the MoO_3–TiO_2 catalyst at 100°C, a sharp singlet signal with g = 2.002 was obtained, as shown in Fig. 4. Thus, the triplet signal with g = 2.019, 2.009, and 2.003 can be ascribed to O_2^-, and the sharp singlet signal with g = 2.002 to O^-. This signal of O^- is similar to those of Setake and Kwan (*9*) and of Ishii and Matsuura (*8*) but does not agree with the results of Shvets and Kasansky (*7*) and of Tench and Lawson (*10*). This is presum-

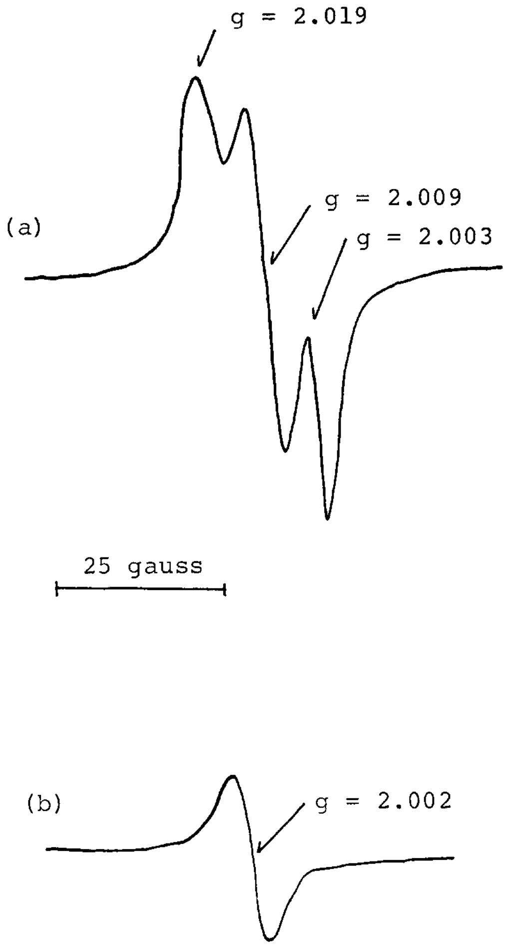

FIG. 4. ESR spectrum of adsorbed oxygen species. (a) O_2 adsorption on MoO_3-TiO_2 (1:99) at 25°C. (b) N_2O adsorption on MoO_3-TiO_2 (1:99) at 150°C.

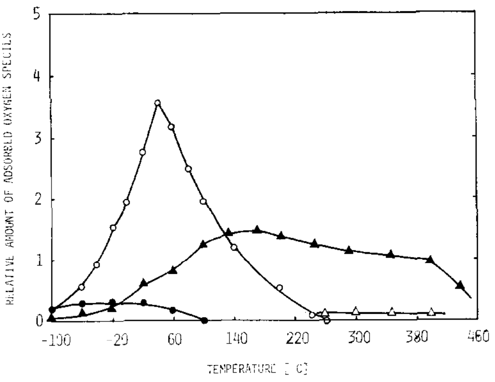

FIG. 5. Effect of temperature on the amount of adsorbed oxygen species. ○: O_2^- on anatase TiO_2, △: S_1 on anatase TiO_2, ●: O_2^- on MoO_3–TiO_2 (1:99), ▲: O^- on MoO_3–TiO_2 (1:99).

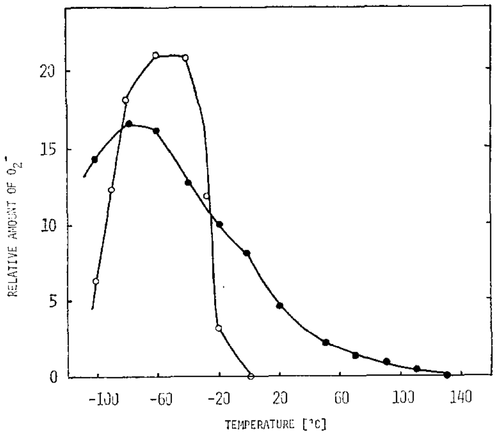

FIG. 6. Effect of temperature on the amount of O_2^- ion. ○: MoO_3–SiO_2 (1:9), ●: MoO_3–Al_2O_3 (2:9).

ably because of the differences in the environment of the adsorption site and in the pretreatment of the catalyst. Figure 5 shows the effect of temperature on the amount of adsorbed oxygen species on the MoO_3–TiO_2 and anatase titania. In the case of anatase titania, there appeared only one adsorbed oxygen species O_2^- which showed the maximum amount at 50°C and disappeared at 230°C. A symmetrical line S_1 with $g = 2.003$ shown in Fig. 5 is attributed to the localization of a conduction electron by the adsorbed oxygen (*11*). In contrast to the case of anatase titania, the MoO_3–TiO_2 catalyst showed the maximum amount of O_2^- at -20°C and this ion disappeared at 100°C with formation of a great amount of O^- which showed a maximum at 150°C. This result suggests that these oxygen species are not formed on titanium ions but on molybdenum ions. As previously shown in Fig. 3, Mo^{5+}(B) formed in MoO_3–TiO_2 catalyst is easily oxidized. Therefore, the following Reaction (a) can be assumed to proceed on this catalyst surface at higher temperatures.

$$O_2(g) \xrightarrow{e} O_2^- \xrightarrow{e} 2O^- \xrightarrow{2e} 2O^{2-} \qquad (a)$$

This O^{2-} combines with molybdenum ion to form Mo^{6+}. The results in the case of MoO_3–Al_2O_3 (2:9) and MoO_3–SiO_2 (1:9) are also shown in Fig. 6. Only one species O_2^- was observed on the MoO_3–Al_2O_3 catalyst, which was in accordance with the result of MoO_3–MgO. This was also similar to the MoO_3–SiO_2 catalyst, but, as Mo^{5+}(B) was formed in this catalyst, absence of O^- on this catalyst is possibly due to the instability of O^- and the rapid progress of the Reaction (a) even at lower temperatures. In contrast to MoO_3–SiO_2 and MoO_3–TiO_2 catalyst, the Reaction (a) seems not to proceed on MoO_3–Al_2O_3 and MoO_3–MgO catalyst because Mo^{5+}(A) on these catalyst is not oxidized even at 450°C.

The result of the vapor-phase oxidation of butadiene by the pulse technique is shown in Table 1. Using helium or air as a carrier gas, butadiene or a mixture of butadiene and air was injected over the oxidized or reduced molybdena catalysts at 380°C by a glass syringe. The reduction was carried out by a pulse of butadiene (5–10 ml) in helium carrier. Comparing the results on the pulse reaction with those on adsorbed oxygen species, it was revealed that molecular oxygen and lattice oxygen O^{2-} are required for the production of maleic anhydride from butadiene, and this lattice oxygen O^{2-} is that formed by the oxidation of Mo^{5+}. Unlike MoO_3–TiO_2 and MoO_3–SiO_2 catalyst, maleic anhydride was not formed by the pulse reaction over MoO_3–Al_2O_3. This can be attributed to the absence of the lattice oxygen O^{2-} which is formed by the oxidation of Mo^{5+}(B).

TABLE 1
OXIDATION OF BUTADIENE BY PULSE METHOD[a]

Catalyst	Carrier gas	Pulse	State of catalyst	Oxygen in pulse	MA yield [%]
MoO_3-TiO_2 (1:3) 0.619 (g)	air	C_4'' 3.0 ml	oxidized	none	13.1
	He	C_4'' 1.0 ml + air 7.0 ml	oxidized	O_2	9.2
	He	C_4'' 1.0 ml + air 11.0 ml	oxidized	O_2	21.0
	He	C_4'' 1.0 or 3.0 ml	oxidized	none	negligible
	He	C_4'' 1.0 ml + air 7.0 ml	reduced	O_2	negligible
MoO_3-SiO_2 (1:9) 1.000 (g)	air	C_4'' 3.0 ml	oxidized	none	7.9
	He	C_4'' 1.0 ml + air 9.0 ml	oxidized	O_2	3.9
MoO_3-Al_2O_3 (1:2) 1.010 (g)	air	C_4'' 3.0 ml	oxidized	none	negligible
	He	C_4'' 1.0 ml + air 9.0 ml	oxidized	O_2	negligible
	He	C_4'' 1.0 ml + air 9.0 ml	reduced	O_2	negligible

[a] Reaction temp: 380°C, carrier gas: 490 NTP ml/min, C_4'': butadiene.

Reactivity of O_2^- Ion

In a previous paper (*12*), the formation of CO_2 and the anhydride formation over titania–oxide with VA or VIB group element catalysts was proved to follow the Langmuir–Hinshelwood mechanism instead of the redox pathway: the rate-determining step of CO_2 formation was a surface reaction of an adsorbed oxygen molecule and butadiene. The first step of maleic anhydride formation was an addition reaction of an adsorbed oxygen molecule to an adsorbed butadiene species. Over these catalysts, the reaction order of butadiene in CO_2 formation was zero and that of oxygen was inversely proportional to the electronegativity of the added element. Table 2 shows the maximum amount of O_2^- measured by ESR and the rate of butadiene consumption at 380°C over these catalysts. Thus, the amount of adsorbed oxygen molecule during the oxidation agrees with the order of the maximum amount of O_2^-. As shown in Table 2, the catalytic activity was also found to be enhanced with increase in the amount of O_2^-. The Bi_2O_3–TiO_2 catalyst showed a higher rate of butadiene consumption relative to the amount of O_2^-, because Bi_2O_3 cannot dissolve in titania and free Bi_2O_3 is very easily reduced. Thus it seems probable that the adsorbed oxygen molecule is present as O_2^- or a negatively charged oxygen molecule on the catalysts during the oxidation rather than as a physically adsorbed oxygen molecule or other molecular oxygen species without charge transfer. In liquid-phase oxidation of butadiene initiated by a radical reagent, an addition product $(CH_2—CH=CH—CH_2—O_2)_n$ was formed (*13*). As O_2^- is a radical, a reaction similar to that in liquid-phase oxida-

TABLE 2
OXIDATION OF BUTADIENE OVER TiO_2/VA-GROUP CATALYSTS[a]

Catalyst (mole ratio)	E.N.	Surface area [m^2/g]	Max. amount of adsorbed O_2^-/[m^2-cat]	Rate of C_4'' consumption [g mole/m^2-cat hr]
TiO_2–P_2O_5 (18:1)	2.1	229	0.448	2.325×10^{-3}
TiO_2–As_2O_3 (18:1)	2.0	35	0.379	1.098×10^{-3}
TiO_2–Sb_2O_3 (18:1)	1.9	29	0.069	0.206×10^{-3}
TiO_2–Bi_2O_3 (18:1)	1.9	52	0.039	1.832×10^{-3}

[a] E.N.: electronegativity of VA group element (Pauling). Oxidation of C_4'': C_4'' 1.5 vol % in air at 380°C.

tion is expected on the catalyst surface in vapor-phase oxidation, but in this case an addition product such as that in liquid-phase oxidation must be destroyed rapidly to give CO_2 or maleic anhydride with the aid of O^{2-}.

Structure of Selective O^{2-} Ion

Table 3 shows the result of the oxidation of butadiene over various titania-supported catalysts. Among these oxides, P_2O_5, As_2O_3 (or As_2O_5), Ta_2O_5, WO_3, and MoO_3 have a double bond between oxygen and element M such as $M{=}O^{2-}$. Other oxides and titania do not have such a double bond but only σ-bond type lattice oxygen $M—O^{2-}—M$. It is interesting to note that maleic anhydride formation was observed in the oxidation only over the catalysts which have a double bond type lattice oxygen. This result reveals the peculiar reactivity of double bond type lattice oxygen in the oxidation of butadiene to the anhydride, thus suggesting that the selective O^{2-} formed by the oxidation of Mo^{5+}(B) is a double bond type oxygen $Mo^{6+}{=}O^{2-}$. Tarama *et al.* (*14*) explained the activity of V_2O_5 catalyst in oxidation reactions as a reactivity of double bond type lattice oxygen $V^{5+}{=}O^{2-}$ which projects out of the catalyst surface. By analogy with V_2O_5 catalyst, oxygen in $Mo^{6+}{=}O^{2-}$ may play a role in the selective oxidation of butadiene as an oxygen species O^{2-} over MoO_3–TiO_2 and MoO_3–SiO_2 catalyst.

Reduction and reoxidation of MoO_3–TiO_2 catalyst was then investigated by ir. As titania has no absorption band at 1100–400 cm^{-1}, the appearance or disappearance of an ir absorption band can be ascribed to a change in the molybdena. Assuming that S_1 or S_2 is a peak area of $Mo^{6+}—O^{2-}—Mo^{6+}$ ir absorption at about 865 cm^{-1} or of $Mo^{6+}{=}O^{2-}$ at about 990 cm^{-1} (*15*) and S is S_2/S_1, we compared S before and after reduction and calculated $X = S(\text{after})/S(\text{before})$. If $X < 1$, it can be possible that the double bond oxygen is reduced easier than the σ-bond oxygen. As shown in Fig. 7, the shift of ir peak position by the reduction is small, indicating that change of the molecular absorption constants of these peaks is negligible. Figure 7 also shows $X < 1$. Thus, the double bond oxygen was proved to be reduced easier than the σ-bond oxygen. It can therefore be concluded that double bond type lattice oxygen $Mo^{6+}{=}O^{2-}$, which is formed by the oxidation of Mo^{5+}(B) and projects out of the catalyst surface, plays an important role as a selective oxygen species O^{2-} in the oxidation of butadiene to maleic anhydride.

In conclusion, the nature of the Mo^{5+}

TABLE 3

OXIDATION OF BUTADIENE OVER VARIOUS CATALYSTS[a]

Catalyst (mole ratio)	Wt [g]	Temp. [°C]	Conversion of C_4'' [%]	Yield of (CO_2 + CO) [%]	Yield of MA [%]
TiO_2 (anatase)	0.600	381	25.5	24.6	0.00
TiO_2–P_2O_5 (18:1)	0.418	396	27.2	25.2	0.90
TiO_2–As_2O_3 (18:1)	0.488	465	9.7	9.1	0.61
TiO_2–Sb_2O_3 (18:1)	0.527	476	0.51	0.51	0.00
TiO_2–Bi_2O_3 (18:1)	0.787	460	8.2	8.2	0.00
TiO_2–ZnO (9:1)	0.818	449	69.6	64.1	0.00
TiO_2–Ta_2O_5 (18:1)	0.640	431	46.6	27.5	1.34
TiO_2–P_2O_5 (2:1)	0.185	461	41.4	34.9	3.8
TiO_2–WO_3 (3:1)	0.741	453	38.3	30.3	3.6
TiO_2–MoO_3 (3:1)	0.682	364	68.6	32.8	28.4

[a] C_4'': 1.5 vol % in air, F: 500 NTP ml/min.

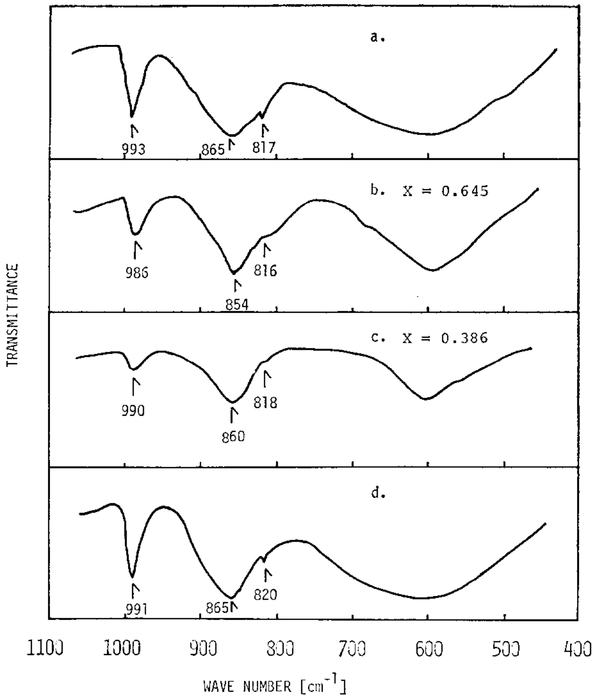

FIG. 7. IR spectra of MoO_3-TiO_2 catalyst (MoO_3 75 mole %). a: nontreated, b: reduced with hydrogen at 450°C for 5 min, c: reduced with hydrogen at 450°C for 20 min, d: reoxidized with oxygen at 450°C for 20 min.

formed when molybdena is supported on a carrier is remarkably affected by the property of carrier. Mo^{5+}(B), which is easily oxidized by oxygen, showed good selectivity to maleic anhydride formation in the oxidation of butadiene. O_2^- and $Mo^{6+}=O^{2-}$ formed by the oxidation of Mo^{5+}(B) are required for the production of maleic anhydride.

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