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Hydrocarbon Species Selective for Maleic Anhydride Formation in Vapor-Phase Oxidation of Butadiene Over Supported Molybdena Catalyst

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Vapor-phase oxidation of butadiene over molybdena–titania as catalyst has been investigated with reference to the nature of adsorbed butadiene species selective for maleic anhydride formation. Maleic anhydride is formed from butadiene species adsorbed on Mo^{5+} in contrast with carbon dioxide from the species on Ti^{4+}. Thus, the selectivity was found to be strongly influenced by the nature of metal ion on which butadiene is adsorbed. Mo^{5+} is "softer" than Ti^{4+}, and for different dienes the diene for which the energy level of the lowest vacant antibonding molecular orbital is lower gave a higher rate of anhydride formation. Therefore, it was concluded that back-donation of electrons from the metal ion to adsorbed butadiene species or softness of the metal ion has a strong effect on the selectivity.

The results are also discussed with the aid of quantum chemical calculations of the adsorbed butadiene species. The first step of maleic anhydride formation was assumed to be addition of radical-like oxygen species to the end of adsorbed butadiene species through a radical and ionic mechanism, in contrast with carbon dioxide formation through an ionic mechanism.

INTRODUCTION

It has long been recognized in heterogeneous catalysis that selectivity can be remarkably affected by the nature of adsorbed reactant species. This is true in the vapor-phase oxidation of hydrocarbons over metal oxides, where the selectivity is markedly dependent on the nature of adsorbed hydrocarbon and oxygen species. In catalytic oxidations, there are few reports about the selective hydrocarbon species with the exception of the π-allyl intermediate in the oxidation of propylene or in the oxidative dehydrogenation of butene over Cu_2O or MoO_3–Bi_2O_3 (*1–3*).

In previous studies on the vapor-phase oxidation of butadiene over supported molybdena catalysts, it has already been shown that the selectivity to maleic anhydride formation is strongly affected by the kind of oxygen species formed on the molybdenum ion and that double bond type lattice oxygen $Mo^{6+}{=}O$ plays an important role as a selective oxygen species. Mo^{5+} was also found to be an active site for the oxidation (*4*). In this paper, selectivity in the oxidation of butadiene over molybdena–titania has been investigated by kinetic measurements, by competitive adsorption and by quantum-chemical calculations. The nature of the selective butadiene species and the reaction mechanism for maleic anhydride formation are then discussed.

EXPERIMENTAL METHODS

Catalytic oxidation of butadiene was carried out using a conventional flow microreactor at a pressure of 1 atm as described previously (*4*). As reactants, air, nitrogen, very pure pentenes, isoprene and butadiene were used in all experiments. Air was purified by passing through silica-gel and a soda-lime tower. Molybdena–titania and titania–VA or VIB group element catalysts were also prepared by the same method as described before (*4*). As sources of P_2O_5, Sb_2O_3, Bi_2O_3, WO_3 and Cr_2O_3, 85 wt% H_3PO_4, extra pure Sb_2O_3, $Bi(NO_3)_3 \cdot 5H_2O$, ammonium tungstate and $Cr(NO_3)_3 \cdot 9H_2O$ were used. The gaseous effluent from the reactor was analyzed by gas chromatography. Propylene carbonate on Celite 545 and molecular sieve 13X were used as separating columns. 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 using a pH meter. Scarcely any monocarboxylic acids were formed in the oxidation of these hydrocarbons. The amount of Mo^{5+} formed in the catalyst was measured by ESR with Mn^{2+}/MgO as an internal standard.

Results and Discussion

Active Site in the Oxidation Over MoO_3–TiO_2 Catalyst

It was already shown in a previous paper (*4*) that the selectivity to maleic anhydride formation over MoO_3–TiO_2 catalyst was remarkably influenced by the composition of the catalyst, in contrast with SiO_2, Al_2O_3 and MgO carriers. This suggests the special participation of titanium ions in the oxidation of butadiene over MoO_3–TiO_2 catalyst. Table 1 shows the selectivity to be independent of the contact time in the oxidation of butadiene over MoO_3–TiO_2(1:3) catalyst, thus indicating that successive oxidation of maleic anhydride does not occur, the anhydride and carbon dioxide being formed through different reaction paths.

TABLE 1

Effect of Contact Time on the Selectivity[a]

W/F [g-cat. hr/g-mol]	Conversion (%)	Selectivity to (CO$_2$ + CO) (%)	Selectivity to Maleic anhydride (%)
0.3264	30.6	45.8	45.6
0.3903	39.8	46.6	43.2
0.4723	51.0	45.0	39.7
0.6070	65.6	44.3	40.0
0.7822	77.9	48.5	42.2
1.0382	92.4	44.3	42.7

[a] Cat., MoO_3-TiO_2 (1:3); butadiene, 1.5 vol% in air; temp, 380°C (reactor).

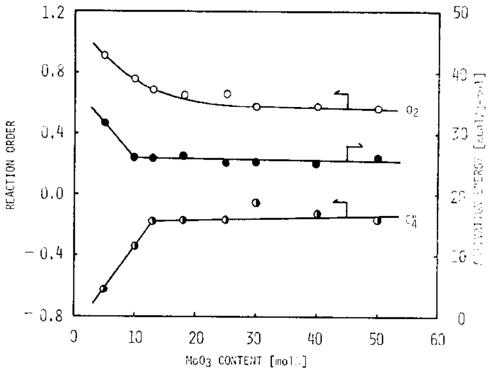


FIG. 1. Correlation between content of MoO_3 and kinetic parameters for maleic anhydride formation reaction. Reaction order, at 365°C; Activation energy, at 350–390°C.

For the purpose of investigating the nature of active sites for maleic anhydride and carbon dioxide formation, butadiene was oxidized by a differential method over various MoO_3–TiO_2 catalysts and the results obtained were described by the power rate law. Apparent activation energies and reaction orders of butadiene and oxygen for the anhydride or carbon dioxide formation are shown in Fig. 1 or 2, respectively. The kinetic parameters for maleic

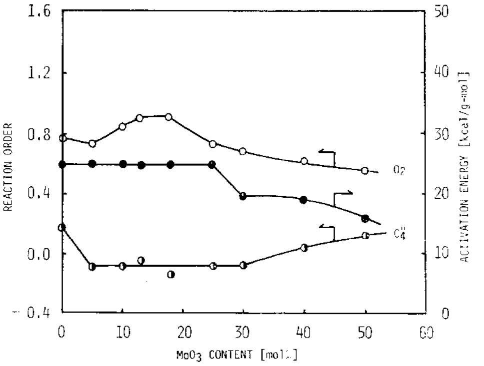


FIG. 2. Correlation between content of MoO_3 and kinetic parameters for carbon dioxide formation reaction. Reaction order, at 365°C; activation energy, at 350–390°C.

anhydride formation remained constant over the catalysts of 13–50 mol% MoO_3 content in contrast with those of 5–10 mol% MoO_3. This provides powerful evidence for the homogeneity of the active sites for maleic anhydride formation. In the case of the latter catalysts, the distance between active Mo^{5+} sites on the surface seems to be fairly large, which may give rise to some enhancement of the activation energy and of the amount of adsorbed butadiene species. Therefore, it can presumably be concluded that the nature of each active site for maleic anhydride formation is homogeneous over these MoO_3–TiO_2 catalysts.

In the case of carbon dioxide formation, the reaction order of oxygen shows a small perturbation over the 5–25 mol% MoO_3 catalysts but the order of butadiene and the activation energy is constant. This also suggests the homogeneity of the sites for carbon dioxide formation over the catalysts. However, when the content of MoO_3 attains 30 mol% and the presence of free MoO_3 becomes observable by X-ray analysis (*4*), the kinetic parameters change noticeably. Therefore, it seems that the active sites for carbon dioxide formation over the catalysts of 5–25 mol% MoO_3 do not agree with those on pure MoO_3. Thus, the catalyst in which free MoO_3 is not present was investigated extensively with reference to the sites for carbon dioxide formation. In contrast with maleic anhydride formation, there is no sudden increase in the activation energy and decrease in the reaction order of butadiene over the catalysts of lower MoO_3 content. This suggests that the distance between the sites for butadiene and oxygen adsorption is not so large as in the case of maleic anhydride formation on these catalyst surface.

In order to determine the sites for butadiene and oxygen adsorption, oxidation of butadiene was carried out over the catalysts consisting of titania and VA or VIB group element using a differential reactor. The kinetic parameters for carbon dioxide formation were plotted vs $-\Delta H_O$[kcal/O atom] or enthalpy change per oxygen atom in the oxide formation at the standard state as shown in Fig. 3. Increasing $-\Delta H_O$ results in a decrease of the reaction order of oxygen or in an enhancement of the amount of adsorbed oxygen species during the oxidation, which is also in good agreement with the activation energy. Moro-oka, Morikawa and Ozaki (*5*) studied the complete oxidation of olefins over various oxide catalysts and concluded that the reaction order of oxygen decreases in inverse proportion to $-\Delta H_O$ in contrast with that of olefin and the activation energy. Therefore, it is very possible that the oxygen species does not form on the titanium ion but does so on these added elements or the nature of sites for oxygen adsorption on titania changed according to $-\Delta H_O$. At any rate, the sites for oxygen adsorption inherent to titania seem to disappear by addition of a small amount of the oxides.

Figure 3 also shows the reaction order of butadiene to be independent of $-\Delta H_O$, thus suggesting that butadiene is adsorbed on titanium ions. It is very difficult to assume that butadiene can be adsorbed on bismuth, antimony and phosphorus ions as strongly as on molybdenum, tungsten and chromium ions, which also gives powerful evidence for the above conclusion. A similar regularity was also observed over the catalysts containing 5 atom%/Ti atom of the elements.

Figure 4 shows the result of temperature programmed desorption, in which various

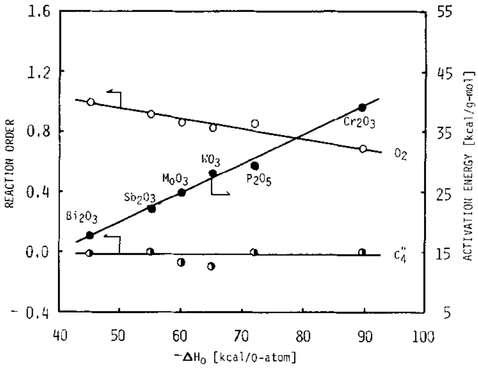


FIG. 3. Relationships in carbon dioxide formation. Reaction order, 365°C; activation energy, at 350–390°C; content of the added element, 10 atom%/Ti atom.

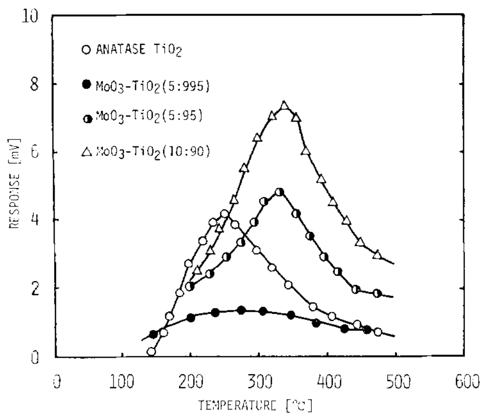


FIG. 4. Temperature programmed desorption. Cat., 1.00 g; He, 30 NTP ml/min; cell current, 120 mA; rate of temperature rise, 4.4°C/min.

catalysts were evacuated at 200°C for 1 hr and butadiene was adsorbed at 100°C. After the evacuation of the catalysts at 100°C for 30 min, temperature was raised at a fixed rate with a constant flow of helium. By gas chromatographic analysis carbon dioxide was observed in the effluent but not butadiene. Thus, adsorbed butadiene species seem to react with oxygen species on the catalysts by the temperature rise forming carbon dioxide.

As shown in Fig. 4, the response was abruptly decreased by addition of only 0.5 mol% MoO_3 to anatase titania and further addition resulted in the appearance of a new peak. It has been generally accepted in oxidation reactions that catalytic activity is strongly affected by the strength of the metal-oxygen bond; breaking the bond is the most important step for the reaction. The different peak temperatures can therefore be attributed to different strengths of the bond. Thus, it can be concluded that oxygen species inherent to titania disappeared by the addition of MoO_3 with alternative formation of oxygen species characteristic to MoO_3. In a previous paper (*4*), ESR studies on oxygen species adsorbed on MoO_3-TiO_2 catalyst revealed that oxygen is adsorbed on Mo^{5+}, which also provides strong evidence for the above conclusion. Thus, carbon dioxide was found to be formed by the reaction of butadiene species adsorbed on Ti^{4+} ions with oxygen species formed on molybdenum ions over MoO_3-TiO_2 catalyst.

For the purpose of determining the number of Mo^{5+} ions participating in the rate controlling step of maleic anhydride or carbon dioxide formation, the amount of surface Mo^{5+} was determined by means of ESR (*6*). Correlation between this amount and the rate of maleic anhydride or carbon dioxide formation as measured by a differential method is shown in Fig. 5. These rates were determined at 365°C and a butadiene concentration of 1.5 vol% in air. Rates of carbon dioxide formation over the catalysts (MoO_3, 30, 40 and 50 mol%) are not taken into account because of the different active sites for carbon dioxide formation from those on the other catalysts. We can see a linear relationship existing between the rate and the amount of Mo^{5+}, which suggests participation of one Mo^{5+} ion in carbon dioxide formation in the rate controlling step.

In Fig. 5, a sudden increase in the rate of maleic anhydride formation is also observable with enhancement of the amount of Mo^{5+}. This may indicate that more than one Mo^{5+} takes part in the formation of maleic anhydride at the rate controlling

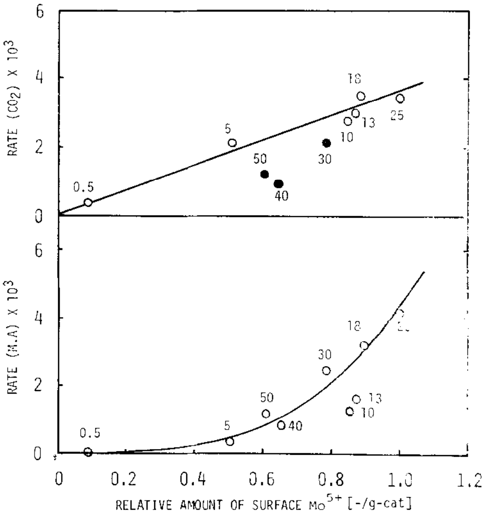


FIG. 5. Rate of carbon dioxide or maleic anhydride formation vs relative amount of Mo^{5+} on the catalyst surface. Rate, [g-mol/g-cat. hr]. Each number shows MoO_3 content (mol%) in the catalyst.

step. Ti^{4+} and Mo^{5+} are hard Lewis acids (*7*) and the latter ion is capable of polymerizing olefins (*8*), which suggests that butadiene is strongly adsorbed on the metal ions, adsorbed butadiene species and the intermediate compound being immobile on the surface. Therefore, it can be concluded that the reaction of oxygen species formed on molybdenum ions with butadiene species adsorbed on Ti^{4+} ions forms carbon dioxide, in contrast with butadiene species on Mo^{5+} which leads to maleic anhydride. MoO_3–TiO_2 (MoO_3 18 mol%) in which the presence of free MoO_3 was not observed possesses a maximum surface area and showed the maximum selectivity to (CO_2 + CO) formation (*4*). This also supports the participation of Ti^{4+} in carbon dioxide formation. Thus, the above result clearly demonstrates the dependency of the selectivity to maleic anhydride formation on the nature of adsorbed butadiene species or of the metal ion on which butadiene is adsorbed.

Nature of Adsorbed Butadiene Species and Its Selectivity to Maleic Anhydride Formation

The mechanism of olefin adsorption has long been studied by many investigators (*9*). A competitive adsorption method is very advantageous for investigating the nature of adsorbed olefin species during catalytic reactions. So the nature of adsorbed butadiene species on Mo^{5+} and Ti^{4+} was investigated by a competitive adsorption of butadiene with various pentenes. If the reaction order of butadiene in carbon dioxide or maleic anhydride formation is nearly zero, the rate of the formation from pure butadiene or pentene can be written as r_{oi} as shown in (a).

$$r_{oi} = k_i \frac{K_iC_i}{1 + K_iC_i} f_i(O_2), \tag{a}$$

where k_i	rate constant of surface reaction
K_i	equilibrium constant of adsorption
C_i	concentration of component i in gaseous phase
$f_i(O_2)$	term of oxygen concentration formed on catalyst
$i = 4$ or 5	butadiene or pentene

In the simultaneous oxidation of butadiene and pentene, the rate r will be

$$r = \sum_{i=4}^{5} k_i \frac{K_iC_i}{1 + K_4C_4 + K_5C_5} f_i(O_2). \tag{b}$$

If $K_4, K_5 \gg 0$ or $K_iC_i \gg 1$, the following equations can be derived from (a) and (b).

$$r_{oi} = k_i f_i(O_2), \tag{c}$$

$$r = \sum_{i=4}^{5} k_i \frac{K_iC_i}{K_4C_4 + K_5C_5} f_i(O_2). \tag{d}$$

Thus, Eq. (e) is obtained from (c) and (d).

$$\frac{r_{o4} + r_{o5}(C_5/C_4)}{r} = 1 + (K_5/K_4)(C_5/C_4). \tag{e}$$

The relative equilibrium constant of adsorption (K_5/K_4) can be determined by a linear plot of (e).

Oxidation of butadiene or 1-pentene was carried out at 362°C over MoO_3–TiO_2 (MoO_3 18 mol%) catalyst by means of a differential method and the resulting reaction order of the hydrocarbons in maleic anhydride formation was 0.16 (butadiene) or −0.07 (1-pentene), respectively. That of butadiene in carbon dioxide formation over anatase titania was 0.17 at 382°C. Thus, the assumption of the competitive adsorption method was sufficiently satisfied.

In Fig. 6, the result of the competitive adsorption of butadiene with pentene in carbon dioxide formation over anatase titania is shown as a linear plot of Eq. (e). The relative equilibrium adsorption constants of pentenes are as follows:

2-methyl-2-butene (1.950) > 1-pentene (1.640) >
3-methyl-1-butene (1.541) > butadiene (1.000).

This order is in good agreement with that on 1.3.5-trinitrobenzene (TNB) (*10*). The following sequence was obtained on Mo^{5+} in maleic anhydride formation (Fig. 7):

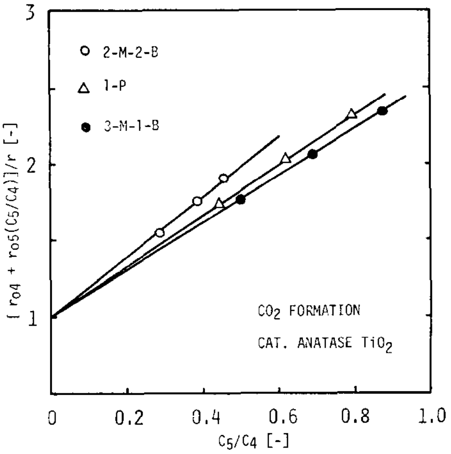


FIG. 6. Competitive adsorption of pentenes with butadiene in carbon dioxide formation. Reaction temp, 382°C; butadiene or pentenes, 1–6 vol% in air.

2-methyl-2-butene (2.125) > 2-methyl-1-butene
(1.675) > 3-methyl-1-butene (1.580) >
1-pentene (1.425) > butadiene (1.000).

The order of 1-pentene and 3-methyl-1-butene is inverted but the tendency of the adsorption strength almost agrees with that on TNB, which is in accordance with the result on Ti^{4+}. The equilibrium composition of 2-methyl-2-butene or 2-methyl-1-butene in pentenes at 400°C is 51.5 or 22.3%, respectively. If the metal ions adsorb these pentenes with formation of carbonium ions, the equilibrium adsorption constant of 2-methyl-1-butene can be expected to be larger than that of 2-methyl-2-butene. But this is not consistent with our results. Thus, the above results provide good evidence for the adsorption of butadiene and pentenes on Mo^{5+} and Ti^{4+} with formation of slightly positively charged π-complexes instead of carbonium ions.

Misonō (*11*) calculated the value of a parameter (designated X or Y) for hardness or softness of a metal ion M^{n+} using the electronegativity of the element M, its ionization potentials and the ionic radius of M^{n+}, i.e., hardness or softness of a metal ion increases in proportion to X or Y, respectively. The X and Y values of various metal ions were calculated similarly and the results are Ti^{4+} (X = 12.22, Y = 1.47), Mo^{4+} (13.56, 2.58), Mo^{5+} (20.62, 2.62) and Mo^{6+} (28.37, 1.36). It is apparent that the equilibrium adsorption constant or nature of adsorbed olefin species is a function of X and Y. In the case of Ti^{4+}, X is large relative to Y, thus suggesting that pentenes are adsorbed on Ti^{4+} by donating their π-electrons to the ion. It is of interest to note that Mo^{4+} and Mo^{5+} are softer than the other metal ions. Disproportionation of olefin is a symmetry forbidden process according to the Woodward-Hoffmann rules, but the symmetry restrictions can, in theory, be totally removed by introducing into the system the appropriate transition metal complex such as Mo^{4+} which injects an electron pair into an antibonding ligand combination (*12*). This shows that back-donation of electrons from Mo^{4+} to adsorbed olefin species occurs (*13*). Mo^{5+} has one 4*d*-electron while Ti^{4+} has an electronic structure similar to that of argon. Therefore, it is very likely that Mo^{5+} is also able to inject an electron into an antibonding

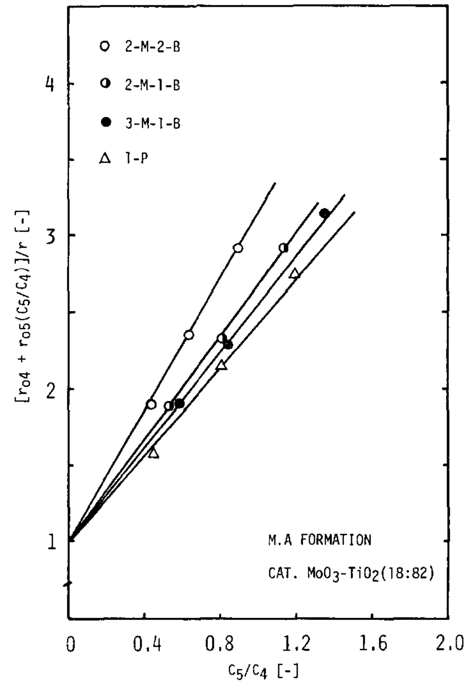


FIG. 7. Competitive adsorption of penetenes with butadiene in maleic anhydride formation. Reaction temp, 362°C; butadiene or pentenes, 1–6 vol% in air.

molecular orbital of adsorbed pentene and butadiene species in contrast with Ti^{4+}, though its amount is smaller than that donated from the adsorbed species.

The back-donation seems to occur more easily in the case of olefins for which the energy level of the lowest vacant antibonding molecular orbital is lower. The energy levels of butadiene and isoprene are 3.4 and 3.2 eV (*14*). When these dienes are oxidized by gaseous oxygen over MoO_3–TiO_2 catalyst, they possibly form various maleic anhydrides through the same reaction mechanism. If the back-donation is favorable to maleic anhydride formation, the rate of dicarboxylic acid formation can, therefore, be expected as follows: butadiene (maleic anhydride) > isoprene (citraconic anhydride). Thus, the dienes were oxidized over MoO_3–TiO_2 (MoO_3 18 mol%) catalyst by a differential method and the kinetic parameters obtained are shown in Table 2 with the rate of dicarboxylic acid and of carbon dioxide formation.

We can see that the apparent activation energy of maleic anhydride formation from butadiene is approximately equal to that of citraconic anhydride from isoprene, which suggests that these anhydrides are formed according to the same reaction mechanism. But there is a great difference between the rates of formation of these anhydrides, which can be attributed to different surface reaction constants or to different frequency terms. According to the activated complex theory, the concentration of activated complexes suitable for maleic anhydride formation seems to be very much larger than that for citraconic anhydride on the catalyst surface. The energy level of the lowest vacant antibonding molecular orbital of the diene will affect the concentration of the activated complex and its reactivity with oxygen species. Even if some citraconic anhydride was successively oxidized through abstraction of hydrogen in the methyl group to form carbon dioxide, the rate of maleic anhydride formation is apparently larger than that of citraconic anhydride formation. This result gives evidence for the effect of back-donation on maleic anhydride formation. Thus, butadiene species adsorbed by donation and back-donation of electrons seems to be selective for maleic anhydride formation in contrast with that by only donation.

Reaction Mechanism

By means of the simple Hückel method, the electronic structure of butadiene species was studied with reference to different reactivities with oxygen species. In the ground state, four π-electrons occupy the bonding molecular orbitals (E_1 and E_2) instead of the antibonding orbitals (E_3 and E_4), where E_i means energy level of i-th molecular orbital from the lowest. Assuming that one π-electron occupying the orbital (E_2) is lost by the donation and that one d-electron is injected into the antibonding molecular orbital (E_3) by the back-donation, the mobile bond order P_{ij}, the index of free valence F_i and the π-electron density on carbon atom $D_{\pi i}$ were calculated by the method proposed by Coulson (*15*). The result is shown in Table 3.

When butadiene is adsorbed by donation (D-type butadiene), mobile bond orders between each carbon atom are nearly equal, but C_1 and C_4 carbon atoms are more positively charged than C_2 and C_3 carbon

TABLE 2
OXIDATION OF VARIOUS DIENES[a]

	Dicarboxylic acid				Carbon dioxide			
Diene	α^b	β	E [kcal/g-mol]	Rate × 10^3	α	β	E [kcal/g-mol]	Rate × 10^3
Butadiene	0.16	0.92	31.8	12.52	0.23	1.00	27.1	9.40
Isoprene	0.00	0.52	30.1	1.72	0.10	0.73	28.9	3.21

[a] Cat: MoO_3–TiO_2 (18:82); O_2, 7–21%; diene, 0.5–2.0%; 360–390°C.

[b] α, β: reaction order of diene or oxygen, rate [g-mol/g-cat. hr] at 363°C and diene 1.5% in air.

TABLE 3
THE ELECTRONIC PROPERTIES OF BUTADIENE SPECIES

	P_{12}	P_{23}	F_1	F_2	$D_{\pi 1}$	$D_{\pi 2}$[a]
Ground state	1.894	1.448	0.837	0.391	1.000	1.000
Donation[b]	1.671	1.585	1.061	0.476	0.638	0.862
Donation and back-donation	1.447	1.724	1.285	0.561	1.000	1.000

[a] Each number indicates *i*-th carbon atom from the end of the conjugated system.

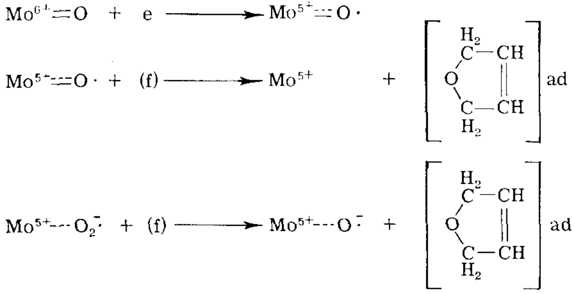
[b] Free valence of carbon atom was calculated assuming that the maximum free valence of the atom is 4.732 though one π-electron of butadiene is lost by its donation.

atoms. On the other hand, each carbon atom of butadiene species adsorbed by donation-and-back-donation (DB-type butadiene) is neutral and the bond between the C_2 and C_3 carbon atoms is approximately equal to a double bond. It is very interesting to note that free valence at the ends of the butadiene species increases remarkably on this kind of adsorption forming a biradical type butadiene species. The electronic nature of butadiene species formed on Ti^{4+} probably looks like that of D-type butadiene, whilst butadiene species on Mo^{5+} looks like a hybrid of D-type and DB-type butadiene species as shown in (f).

$$^{\delta++}\cdot CH_2 \overset{\dots}{=} {}^{\delta+}CH = {}^{\delta+}CH \overset{\dots}{=} {}^{\delta++}CH_2\cdot . \qquad (f)$$

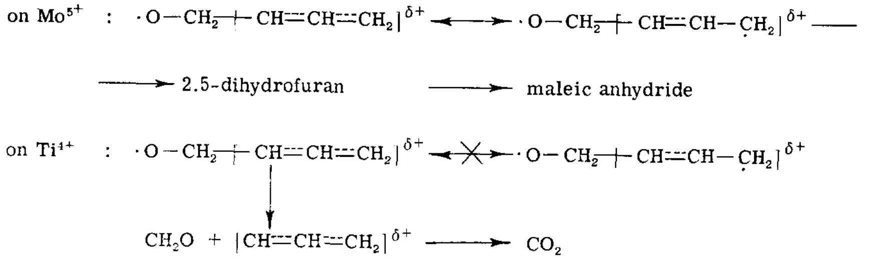
Krylov (*16*) investigated the adsorption of butadiene on NiO–MgO catalyst (Ni^{2+}, $X = 4.75$, $Y = 2.82$) and attributed the intense absorption bands in the 1600 cm^{-1} region to a stretching vibration of the —C=C— bond in *—CH=CH—CH=CH—*. So it may be possible that the butadiene species (f) has a structure Mo^{5+} ---$CH_2 \overset{\dots}{=} CH{=}CH \overset{\dots}{=} CH_2$---$Mo^{5+}$ similar to that described above.

It was already reported that O_2^- and $Mo^{6+}{=}O$ are selective oxygen species, radical-like oxygen species initially reacting with adsorbed butadiene species to form maleic anhydride (*4*). The double bond type lattice oxygen was also found to behave like a radical through electron transfer from adsorbed butadiene into a nonbonding atomic orbital of Mo^{6+} during the oxidation (*17*). Thus, reaction of these radical-like oxygen species with butadiene species on Mo^{5+} is possibly the initial step of the anhydride formation.


(g)
(h)

This reaction mechanism is similar to that for epoxide formation in autocatalytic oxidation of olefins (*18*).

In these reactions, reaction (g) possibly plays an important role of 2.5-dihydrofuran formation in contast with reaction (h), since O_2^- is very unstable on Mo^{5+}. No attempt can be made here to indicate the further mechanism for maleic anhydride formation, but it is apparent that 2.5-dihydrofuran can lead to maleic anhydride. Thus, the first step of maleic anhydride formation from butadiene was found to be an addition of O_2^- or the double bond lattice oxygen to the end of the biradical type butadiene species through a radical and nucleophilic mechanism. In the case of carbon dioxide formation, attack of these oxygen species on D-type butadiene species seems to be a nucleophilic reaction, which is similar to that of the anhydride formation, but the intermediate compound formed is easily destroyed presumably with scission of the carbon chain. A more detailed explanation is given below for the different reactivities of intermediates.



The intermediate compound on Mo^{5+}, which is formed by addition of the oxygen species to the biradical type butadiene, has more than two but less than three π-electrons in the carbon chain and therefore can be a biradical type structure by resonance of π-electrons. This suggests that 2.5-dihydrofuran can be formed from this intermediate by intramolecular cyclization. On the other hand, such a cyclization reaction is hardly to be expected in the case of the intermediate compound on Ti^{4+} because this has no more than two π-electrons in the carbon chain. Thus, the intermediate on Ti^{4+} seems to lead to carbon dioxide with scission of the C_1–C_2 bond.

In conclusion, the hardness or softness of the metal ion present in the catalyst has been found to have a strong effect on the selectivity to maleic anhydride formation in the vapor-phase catalytic oxidation of butadiene. An oxide of a hard metal ion is not an adequate catalyst for the selective oxidation, but increasing the back-donation seems to result in an enhancement of the selectivity. 2.5-Dihydrofuran has been assumed to be the first intermediate of maleic anhydride formation from butadiene.

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