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Mechanism of Propylene Oxidation over Bismuth Molybdate Revealed by Transient Response Method

I. An Intermediate in the Complete Oxidation of C_3H_6

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The mechanism of the oxidation of propylene over bismuth molybdate has been studied in detail by applying a transient response method at temperatures ranging from 190 to 350°C. It was found that a stable intermediate exists on the surface during the reaction. The intermediate (In) can be formed on the surface in the course of the reduction with propylene without being decomposed. However, it is easily decomposed to CO_2, CO, and H_2O, without producing acrolein, by the reaction without oxygen weakly adsorbed from gaseous oxygen. It is presumed that (In) has a structure similar to that of propylene but with a C/H ratio larger than 0.5. The main reaction path which forms (In) during the reaction involves propylene although it is also formed from acrolein. From the experimental finding that the transient response of the rate of CO_2 formation showed behavior quite similar to that of (In) formation, it is concluded that (In) is the reaction intermediate through which CO_2, CO, and H_2O are formed during the reaction.

INTRODUCTION

Much attention has been focused on research involving intermediates in the oxidation of propylene over bismuth molybdate and, especially, on that involving the intermediate in the formation of acrolein caused by the high selectivity of acrolein whereas the origin of the carbon dioxide formed during the reaction has not been clarified. Even though the mechanism of carbon dioxide formation may be represented by a parallel-consecutive type of pathway from both propylene and acrolein (*1*) and by a consecutive type of pathway from acrolein (*2*, *3*), the arguments for the intermediate in CO_2 formation are not conclusive. The reason seems to be that one cannot directly detect the existence of the intermediate due to the small amount present in the ordinary operating temperature region higher than 400°C. In the present study, lower reaction temperatures and a large amount of catalyst were used in order to obtain a lower selectivity to acrolein and a large amount of adsorbed intermediates on the surface. Furthermore, a transient response method (*4*) was applied to elucidate the reaction pathway in the formation of CO_2, the existence of an intermediate in CO_2 formation, and the nature of the intermediate.

1. EXPERIMENTAL METHOD

The catalyst used in this study was precipitated from an acidified bismuth nitrate solution by mixing an ammonium molybdate solution and ammonia to give a final pH of 5.0 and a bismuth: molybdenum

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atomic ratio of about 1.0. The sample was dried at 135°C for 15 hr and then calcined at 500°C for 3 hr prior to use. The X-ray diffraction analysis and the infrared spectrum of the yellow powder sample obtained indicated that the sample was in the mixed form of α-, β-, and γ-phases (*5, 6*). The BET surface area was 2.5 m^2/g. The activity was stable for many hours of use.

The reactor used consisted of a Pyrex glass tube containing the catalyst the amount of which varied according to reaction temperature used. The tube was immersed in an oil bath or a fluidized bath depending on the reaction temperature used. The temperature of the catalyst bed was always kept uniform within ±0.5°C. Oxygen (O_2 99.9%), helium (He 99.99%), carbon monoxide (CO 99.73%), and carbon dioxide (CO_2 99.99%) from commerical cylinders were purified through a dry ice–methanol trap to remove water vapor. Propylene (C_3H_6 98.5%) from a commercial cylinder was used without further purification. Liquid acrolein (acrolein 90%) and water which were kept at constant temperatures were fed into the reactor by using a microfeeder or by bubbling He through them.

The total flow rate of the gas was kept constant at 160 ± 3 ml(NTP)/min and the composition of the reaction gas was varied by changing the concentration of helium as a diluent. The transient response to the step change in the composition of the He–N_2 mixture was completed within 16 sec for the 49.9-g amount of catalyst at 190°C. The intraparticle diffusion resistance was confirmed to be negligible by examining the rate data for catalysts of different sizes, 12 to 20 and 20 to 40 mesh, at 310°C. The external mass transport effect was also determined to be negligible by examining the rate data at constant W/F (7710 g·min/mol of C_3H_6) with various flow rates and amounts of catalyst. The reaction conditions were chosen in such a way that the total conversion of propylene did not exceed 0.06 in all experiments.

Four gas chromatographs, each kept under different conditions, were used simultaneously to analyze all gas components of the reaction as continuously as possible. A Porapak Q column was used for analyzing hydrocarbons and CO_2 and a Molecular Sieves 5A column was used for analyzing CO, O_2, H_2, and N_2. Three flow-control systems, each of which could provide a constant gas flow rate with different compositions, were prepared so that the transient response experiments could be successively conducted among three different gas mixtures within a few minutes. A more detailed description of the transient response method used in this study can be found elsewhere (*4*).

2. EXPERIMENTAL RESULTS AND DISCUSSION

The response of the component Y in the outlet gas mixture to a step change in the concentration of X in the inlet gas stream is designated as an X–Y response. The following symbols will be used: when X is increased, X(inc.,)–Y; when X is decreased, X(dec.,)–Y; when X is increased from nil, X(inc., 0)–Y; when decreased to nil, X(dec., 0)–Y; when the temperature of the catalyst bed is raised linearly with respect to the elapsed time, T(linear)–Y response.

2.1. Adsorption Behavior of CO_2 and CO

Knowledge of the adsorption behavior of CO and CO_2 is needed to analyze the transient response curves obtained during the oxidation of C_3H_6. For this purpose, the following experiments were performed.

After the catalyst had been treated in a pure He stream at 310°C for 3 hr, carbon dioxide of various partial pressures was introduced into the inlet gas stream without changing the total flow rate, and the CO_2(inc., 0)–CO_2 response was followed.

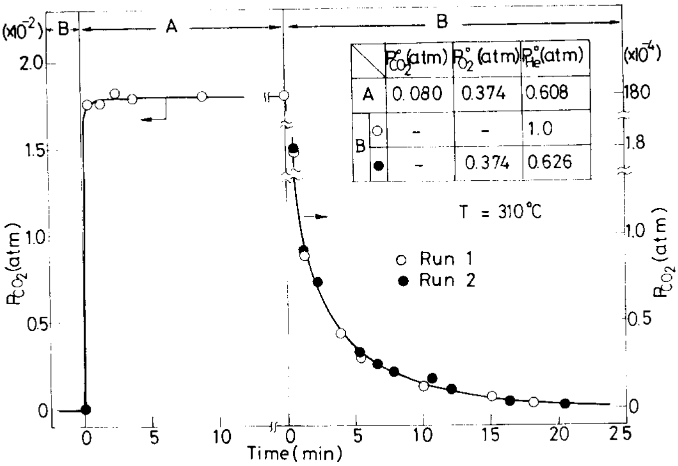


Fig. 1. The CO–CO_2 response.

Subsequently, the carbon dioxide in the inlet gas stream was cut off again by switching over to a stream of either He or a He–O_2 (36.4%) mixture and the CO_2(dec., 0)–CO_2 responses in each case were followed separately. The typical results are presented in Fig. 1. The CO_2(dec., 0)–CO_2 response curves clearly indicate a delay showing that carbon dioxide is adsorbed on the surface and that the mode of response is not affected by the presence of oxygen in the gas phase; this indicates that the adsorbed carbon dioxide is not replaced by the competitive adsorption of oxygen onto the same active sites. The integrated amount of desorbed CO_2 was estimated at various partial pressures of CO_2 and the result gave a linear adsorption isotherm as shown in Fig. 2. This isotherm indicates that only a small amount of CO_2 is adsorbed on the surface. This is the reason why the CO_2(inc., 0)–CO_2 response did not show a clear delay, from B gas to A gas in Fig. 1.

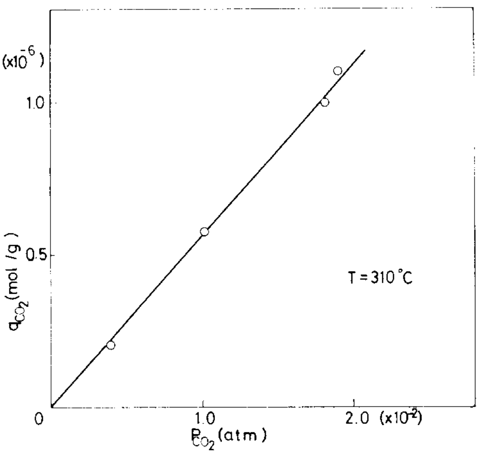
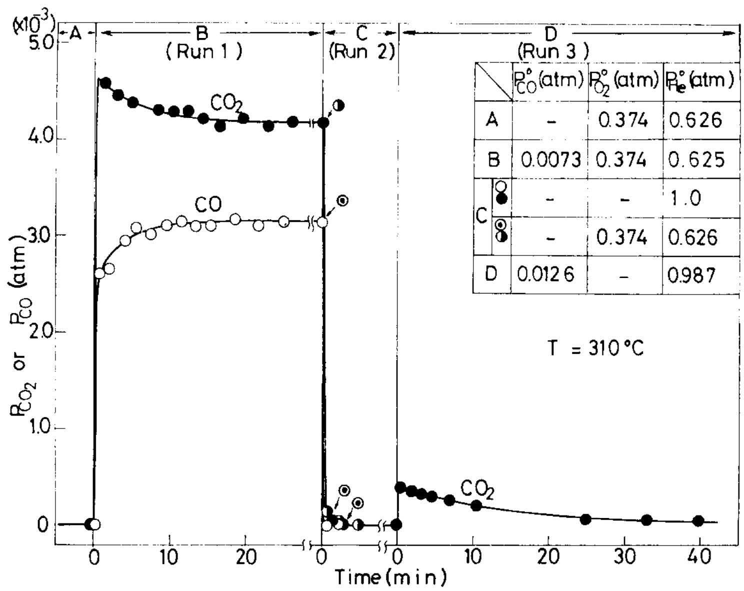


Fig. 2. Adsorption isotherm for CO_2 on Bi–Mo.

The oxidation of CO proceeds on the present catalyst at temperatures higher than 190°C. After the catalyst had been oxidized in a stream of O_2–He for 5 hr, the stream was switched over to a stream of CO(0.73%)–O_2–He (Run 1) and the CO(inc., 0)–CO and –CO_2 responses were followed simultaneously until the reaction attained a steady state. The reaction gas stream was changed to a stream of either pure He or O_2–He (Run 2) and the CO(dec., 0)–CO and –CO_2 responses were again followed. The results are shown in Fig. 3. In Run 1 the CO(inc., 0)–CO_2 response showed an instantaneous maximum followed by a slow decrease (overshoot type). The instantaneous response at the initial stage can be attributed to the rapid desorption of the CO_2 formed. The overshoot-type response suggests that the regeneration step of active surface oxygen from gaseous oxygen is one of the slower



	P°_{CO} (atm)	$P^\circ_{O_2}$ (atm)	P°_{He} (atm)
A	-	0.374	0.626
B	0.0073	0.374	0.625
C ○ ●	-	-	1.0
C ⊙ ◑	-	0.374	0.626
D	0.0126	-	0.987

FIG. 3. CO–CO and CO–CO_2 responses.

steps in the overall reaction, according to Kobayashi's method for estimation of the mechanism of a heterogeneously catalyzed reaction from the mode of transient response curves of products obtained by the concentration jump of reactants (*7*).

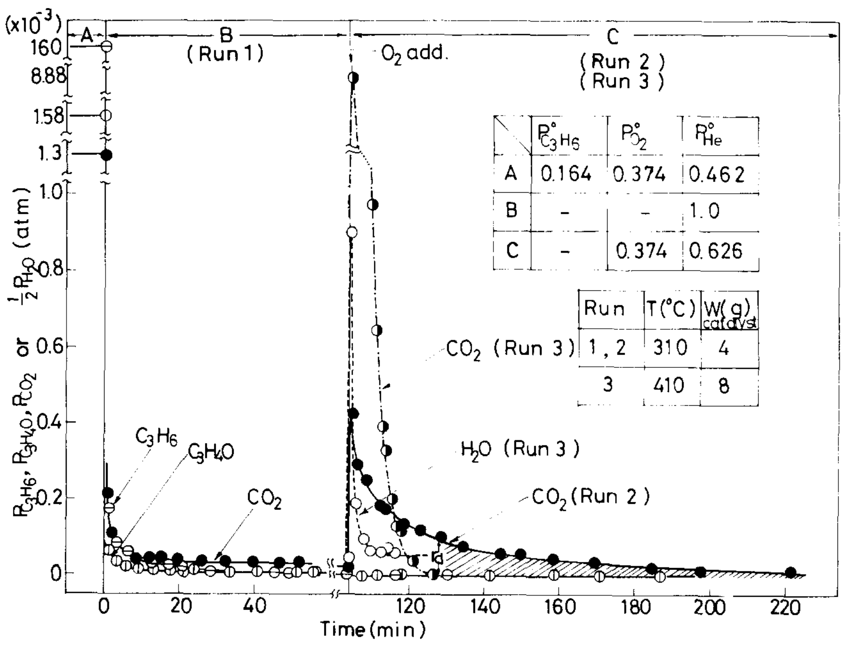
On the other hand, the CO(dec., 0)–CO response in Run 2 showed an instantaneous nil and the CO(dec., 0)–CO_2 response steeply fell down to nil without being affected by the presence of gaseous oxygen. These results strongly indicate that there is neither reversibly adsorbed carbon dioxide nor irreversibly adsorbed carbon monoxide which can react with oxygen and produce carbon dioxide on the surface and that the carbon dioxide formed is desorbed rapidly.

After the CO(dec., 0)–CO_2 response in the O_2–He stream had been completed (Run 2, oxidation of catalyst), the catalyst was exposed to a reducing gas stream of CO(1.26%)–He (Run 3) and the CO(inc., 0)–CO_2 response was followed. The results are shown in Fig. 3. The integrated amount of CO_2 formed in Run 3 corresponds to 2.2×10^{14} oxygen atoms/cm², which is much smaller than the 6×10^{14} atoms of oxygen expected in 1 cm² of surface, regardless of crystallographic structure of the surface. Furthermore, in the reaction temperature region a large amount of oxygen can be expected to diffuse from the bulk of oxide as shown by Keulks (*8*) who estimated that about 500 oxide layers interacted with the oxidation of propylene. This result indicates that the surface oxygen species of the catalyst (probably lattice oxygen) are less active for the oxidation of CO; this is consistent with the experimental results of Matsuura and Schuit (*9*) and Haber and Grzybowska (*10*) who found, respectively, no adsorption of oxygen and no activity in oxygen exchange on very selective Bi–Mo catalysts.

2.2 Formation of a Stable Intermediate in the Complete Oxidation of C_3H_6

After the reaction had attained a steady state, the inlet gas was switched to pure He (Run 1) and the C_3H_6, O_2(dec., 0)–C_3H_4O, –C_3H_6, and –CO_2 responses were followed simultaneously until no desorption of acrolein and propylene could be detected in the effluent gas stream. The catalyst was then exposed to the O_2–He stream (Run 2) and three responses were again followed by carefully monitoring the desorption of H_2O, H_2, CO, aldehydes, and acids. The results obtained are shown in Fig. 4. The response curves (Run 2) show that there is an outflow of an appreciable amount of CO_2 whereas no other products are produced except small amounts of H_2O and CO (the latter is not shown in Fig. 4). The integrated amount of CO_2 formed is estimated to be 1.5×10^{-5} mol/g. There are three possible explanations for the effluent of CO_2 in Run 2: (i) The desorption of CO_2 by the competitive adsorption of oxygen on the active sites which had been occupied by irreversibly adsorbed CO_2 during the reaction; (ii) the reaction between oxygen and irreversibly adsorbed CO which had been formed during the reaction; and (iii) the decomposition of a stable intermediate in the formation of CO_2. The possibility of cases (i) and (ii) can be excluded by the previous observation that the desorption curves of CO and CO_2 were not affected by the presence of gaseous oxygen. Therefore, the effluent of CO_2 in the case of Run 2 can well be attributed to explanation (iii), indicating the presence of an adsorbed intermediate (In) which formed during the course of the reaction and sustained the subsequent treatment in the pure He stream. This idea is further supported by the following transient experiments.

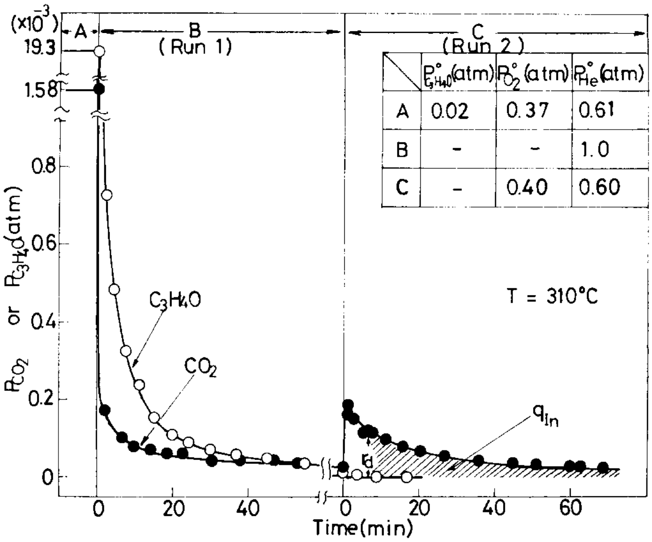
After Run 1 in Fig. 4 had been completed, the temperature of the catalyst bed was raised stepwise from 310 to 410°C in the pure He stream. In this treatment, any components other than small amounts of H_2O and CO_2 were not detected. The stream was then changed to the O_2–He mixture (Run 3) and the O_2(inc., 0)–CO_2 and –H_2O responses were followed simultaneously. The results are shown by Run 3 in Fig. 4. From Run 3, one can clearly recognize the desorption of an appreciable amount of H_2O in contrast to the case at 310°C. This difference between the two temperatures can be attributed to the irreversible adsorption of the H_2O formed because the separate transient response of H_2O obtained by the addition of H_2O to or the removal of H_2O from the inlet pure He



	$P^\circ_{C_3H_6}$	$P^\circ_{O_2}$	P°_{He}
A	0.164	0.374	0.462
B	-	-	1.0
C	-	0.374	0.626

Run	T(°C)	W(g) catalyst
1, 2	310	4
3	410	8

FIG. 4. Decomposition of a stable intermediate formed during the oxidation of C_3H_6.



	$P^\circ_{C_3H_4O}$(atm)	$P^\circ_{O_2}$(atm)	P°_{He}(atm)
A	0.02	0.37	0.61
B	-	-	1.0
C	-	0.40	0.60

FIG. 5. Decomposition of a stable intermediate formed during the oxidation of C_3H_4O.

stream had shown its adsorption to consist of irreversible parts.

The integrated amounts of CO_2 and H_2O formed in Run 3 are estimated to be 1.72×10^{-5} and 2.56×10^{-6} mol/g, respectively. The amount of CO_2 is close to that estimated in Run 2, indicating no difference between the intermediates decomposed in Runs 2 and 3. Since the integrated amount of H_2O formed in Run 3 unfortunately varied due to experimental error and since the amount of irreversibly adsorbed H_2O was not exactly estimated, the C/H ratio for the structure of (In) could not be determined. However, it may be concluded that the ratio is larger than 0.5, taking into account that the amount of H_2O estimated in Run 3 is much smaller than the amount of CO_2 formed and that (In) is also formed from acrolein as described below.

The same transient procedure as used in Runs 1 and 2 in Fig. 4 was employed for the oxidation of acrolein to confirm the formation of (In) from acrolein and the results obtained are shown in Fig. 5. Run 2 in Fig. 5 clearly shows the appreciable amount of desorbed CO_2 with the production of no components other than small amounts of CO and H_2O, indicating the existence of a stable intermediate during the oxidation of acrolein, similar to the case of oxidation of C_3H_6.

In order to know whether or not the intermediate from acrolein was the same as (In) from C_3H_6, the decomposition rates of the intermediates for both oxidations were compared. In Section 2.1, it was concluded that the desorption of CO_2 produced during the oxidation of CO is very rapid. This idea can also be accepted for the oxidation of C_3H_6 based on the observation that the transient response curves of CO_2 formation in the two Run 2's in Figs. 4 and 5 showed an instantaneous maximum at the initial stage of the response without showing a delay (7). Furthermore, using the adsorption isotherm for CO_2 presented in Fig. 2, the amount of CO_2 readsorbed from the gas phase during the course of the decomposition of the intermediate can be easily estimated; the typical amounts of intermediate and readsorbed CO_2 at the maximum point of the response curve in Run 2 of Fig. 4 are estimated to be 1.5×10^{-5} and 2.5×10^{-8} mol of CO_2/g, respectively, where the amount of the intermediate is given for convenience as the amount of CO_2 formed by its decomposition. Therefore, the readsorption of CO_2 is negligible and the desorption rates of CO_2 measured in the response curve of two Run 2's in Figs. 4 and 5 can be considered to be the decomposition rate of the intermediate. From the response curves obtained, one can estimate the decomposition rate of the intermediate (r_d) and the corresponding amounts of the intermediate which are shown by the dashed area in Figs. 4 and 5. The same procedure was also applied to the decomposition response data obtained at various concentrations of C_3H_6 and acrolein and the decomposition rates of the intermediate in both reactions were plotted against the amounts of intermediate. The plots with the same straight line within a 30% error as presented in Fig. 6. This agreement strongly suggests that the intermediate from acrolein is the same as (In) from C_3H_6.

The main route for the formation of (In) during the oxidation of C_3H_6 can be considered by comparing the amount of (In) from C_3H_6 with that from acrolein. The latter is roughly estimated by the following procedure. As described above, the amount of (In) produced during the oxidation of acrolein is easily estimated as the amount of CO_2 formed by decomposing it in a stream with a partial pressure of acrolein. Using the curve obtained, one can estimate the amount of (In) corresponding to the partial pressure of gaseous acrolein produced during the oxidation of C_3H_6; this may be roughly considered as the amount of (In) formed from acrolein ($q_{In}{}^a$). The difference between $q_{In}{}^t$ [the total amount of (In) formed during the oxidation of C_3H_6] and $q_{In}{}^a$ corresponds to the amount of (In) formed from propylene [$q_{In}{}^p$]. The value of $q_{In}{}^p (=2.2 \times 10^{-5}$ mol/g) estimated at $P_{C_3H_6} = 0.222$ and $P_{O_2} = 0.374$ atm and $T = 310°C$ is about eight times the value of $q_{In}{}^a$ ($=0.26 \times 10^{-5}$ mol/g) indicating the main route for the formation of (In) from C_3H_6 during the oxidation of C_3H_6.

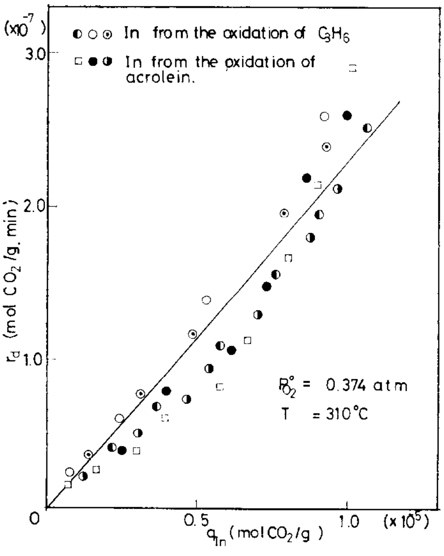
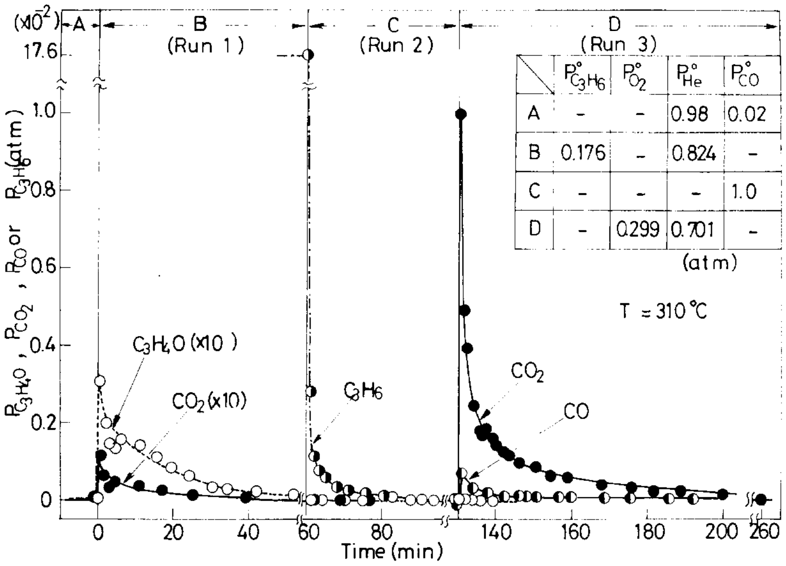


FIG. 6. Decomposition rate of (In) as a function of q_{In}.

2.3. The Nature of (In)

After the catalyst had been reduced in a stream of CO(2%)-He for 2 hr (for the removal of weakly adsorbed oxygen), it was treated successively with a stream of C_3H_6(17.6%)-He until no production of CO_2 was detected as shown by Run 1 in Fig. 7. Run 1 clearly shows that an appreciable amount of acrolein was formed over an extended time whereas only a small amount of CO_2 was produced. The production of acrolein strongly indicates that the catalyst surface still retains some oxygen species which can react with propylene but not with CO. The oxygen species is probably surface lattice oxygen which is active for the formation of acrolein as has been shown by Keulks (*8*) and Wragg, Asmore, and Hockey (*11*).

The reducing gas mixture was then replaced by a pure He stream and the C_3H_6(dec., 0)-C_3H_6 response was followed until the desorption of C_3H_6 was not detected in the effluent gas stream (Run 2). Then the stream was replaced by a stream of O_2(30%)-He (Run 3) and the O_2(inc., 0) -CO_2 and -CO responses were followed



	$P^\circ_{C_3H_6}$	$P^\circ_{O_2}$	P°_{He}	P°_{CO}
A	-	-	0.98	0.02
B	0.176	-	0.824	-
C	-	-	-	1.0
D	-	0.299	0.701	-

(atm)

FIG. 7. Decomposition of (In) formed during the course of reduction with C_3H_6.

simultaneously. The results are shown by Run 3 in Fig. 7. A large amount of carbon dioxide and an appreciable amount of carbon monoxide were desorbed due to the decomposition of (In) formed on the surface during the course of Run 1, whereas products other than water could not be detected. The result clearly indicates that (In) is also an intermediate producing carbon monoxide and is easily decomposed by oxygen which is weakly adsorbed from the gas phase, whereas it could not be decomposed by the surface lattice oxygen as shown in Run 1. Since the course of Run 1 no weakly adsorbed oxygen exists on the surface resulting from the reduction with CO, one can presume that (In) is adsorbed on a surface metal ion and/or on a lattice oxygen.

The integrated amounts of carbon dioxide and carbon monoxide formed in Run 3 are estimated to be 1.3×10^{-4} and 1.4×10^{-5} mol/g, respectively. The sum of both values corresponds to 3.4×10^{15} carbon atoms/cm^2 using a BET surface area of 2.5 m^2/g. This value is about three times the total number of active sites estimated by assuming that the catalyst surface contains 1.2×10^{15} sites/cm^2 for the adsorption of (In), regardless of the crystallographic structure (*12*). This result strongly suggests that (In) is fully adsorbed on every active site with a structure retaining the carbon–carbon bonds in the propylene molecule. Furthermore, the fact that (In) does not produce acrolein can eliminate the possibility of an allylic intermediate structure which has been generally accepted as an intermediate for the formation of acrolein (*13–15*).

A thermal desorption study for the catalyst adsorbing (In) was also performed. After Run 2 in Fig. 7 had been completed (the catalyst surface fully covered with (In)), the temperature of the catalyst bed was decreased in a stepwise fashion to room temperature and then the pure He stream was replaced by a stream of O_2–He. The temperature was then raised at a rate of 2.3°C/min in the same gas mixture to 200°C (Run 3′) and successively to 420°C in pure He instead of the O_2–He mixture (Run 4). The T(linear)–CO_2 response was followed in the course of Runs 3′ and 4 and the results obtained are presented in Fig. 8. During Run 3′, one could not detect any

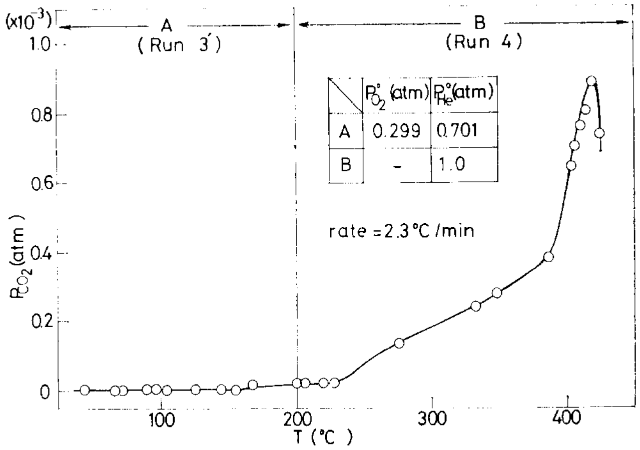


FIG. 8. Decomposition of (In) by heating the catalyst.

components other than a small amount of CO_2 in the effluent gas stream at temperatures near 200°C, in spite of the existence of oxygen in the gas phase. This indicates that (In) cannot be easily decomposed by the reaction with oxygen in this temperature region. On the other hand, Run 4 clearly gave a desorption spectrum of CO_2 with a peak at 420°C resulting from the decomposition of (In), where no components other than appreciable amounts of water and CO were detected. Since there is no oxygen in the gas phase in the course of Run 4, the formation of CO_2 may be attributed to the reaction between (In) and the oxygen rapidly diffused from the bulk of the catalyst to the surface due to the high temperature as has been shown by Keulks (*8*). The result strongly suggests that (In) is unstable at reaction tempera-

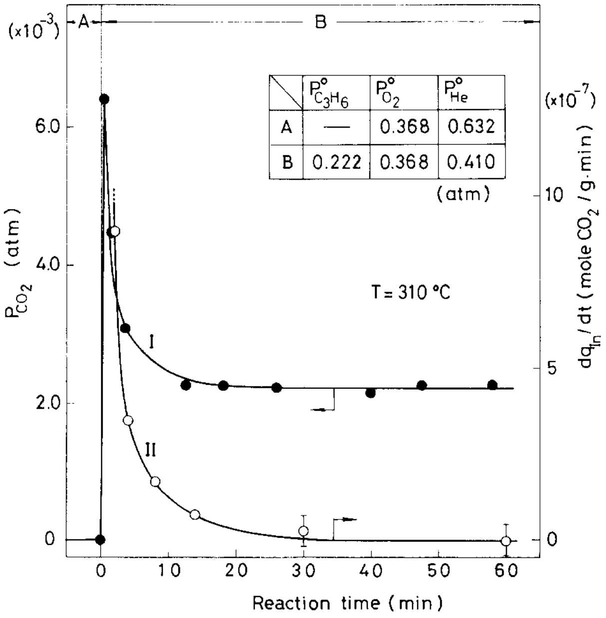
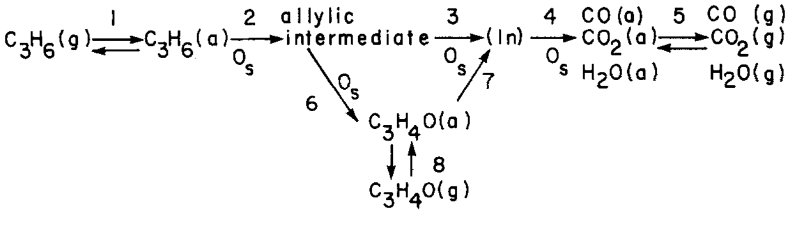


FIG. 9. The C_3H_6(inc., 0)–CO_2 and $-dq_{In}/dt$ responses.

tures higher than 400°C and this view is also supported by the fact that only a small amount of (In) was observed on the surface at the higher temperature.

To know whether the intermediate (In) is an actual intermediate in the complete oxidation of C_3H_6, the following transient response was performed. After the catalyst had been kept in a stream of O_2–He for 5 hr, the stream was replaced by a reaction gas stream and the response of CO_2 and the formation rate of (In) were followed simultaneously. The results are shown in Fig. 9, by curves I and II, respectively. The amount of (In) formed during any time period was roughly estimated by decomposing (In) with the O_2–He stream at the end of the period. This treatment was repeated six times by changing the elapsed time until the reaction reached a steady state. By superposing the results thus obtained, one can draw the response curve of the amount of (In) formed during the period of the unsteady state of reaction, where the amount of (In) is also given for convenience as the amount of CO_2 formed by the decomposition of it in a O_2–He stream. Graphical differentiation of the response curve obtained gives the formation rate of (In) as shown by curve II in Fig. 9. As can be seen from the comparison between curves I and II, both curves show a quite similar behavior. This similarity strongly suggests that (In) is the reaction intermediate through which CO_2, CO, and H_2O are formed during the reaction.

Based on the results obtained so far, one can visualize the reaction mechanism as the following where O_s is lattice oxygen or adsorbed oxygen species.



Step 4 cannot proceed in a gas stream in the absence of gaseous oxygen but rapidly proceeds when a sufficient amount of weakly adsorbed oxygen species are supplied from the gas phase, as shown in Run 3 in Fig. 7. The fact that an appreciable amount of (In) exists on the surface at the reaction steady state suggests that regeneration of the active oxygen species weakly adsorbed from the gas phase is not sufficiently rapid at 310°C. This idea is also supported by the mode of the transient response curves indicating the overshoot type of C_3H_6–CO_2 response as shown by Curve I in Fig. 9. The amount of (In) from Step 3 is about eight times that from Step 7, which was estimated separately from the experiments on the oxidation of acrolein, indicating Step 3 to be the main route. A more detailed kinetic structure for the reaction will be reported later.

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