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Study of Metal Oxide Catalysts in the Olefin Oxidation from their Reduction Behavior

II. Reduction of ZnO with Propylene

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The reduction behavior of ZnO in a stream of propylene was investigated in detail. Propylene consumed the oxidic oxygen of a few lattice layers to produce 1,5-hexadiene, benzene, acetone, and CO_2. The time courses of respective products were, however, not only different from each other but also dependent on the reduction conditions. With varying propylene partial pressure (P_{PR}), the formation of CO_2 was almost unaffected, suggesting that it is responsible to very reactive oxygen such as adsorbed oxygen. The other products showed dependences on P_{PR}. Detailed analyses were carried out for the formation behavior of 1,5-hexadiene which showed a large formation maximum. It was shown that its time course taken under various P_{PR} could be reduced to the same analytical form; the formation rate $= k(Y')^2(Y'_\infty - Y')^2$ where Y' and Y'_∞ denote the amount of consumed oxygen at time $t = t$ and $t = \infty$, respectively. This equation confirms that the increase of the propylene adsorption sites (exposed zinc atoms) combined with the decrease of the surface active oxygen during reduction brings about the rate maximum. The reaction orders of the equation, moreover, give the picture that the rate-determining step of the 1,5-hexadiene formation is associated with the reaction between two adsorbed propylene molecules and two oxidic oxygen atoms.

INTRODUCTION

Previously we reported the reduction of various metal oxides with propylene (*1*). It showed that the rate of propylene conversion, the products, and their selectivity in the initial stage of reduction were well correlated to those for the catalytic oxidation of propylene. This indicates that the reduction reaction reflects well the reduction step of a redox cycle which an oxide catalyst may undergo during the catalytic oxidation. The time courses of reduction, however, were strongly dependent on the kind of metal oxide, suggesting that important information concerning catalytic activity of metal oxides may be extracted from the reduction behavior. Especially interesting was the case of ZnO reduction. Zinc oxide belongs to a group of oxides which can be reduced with propylene by only a few surface lattice layers. The rate of 1,5-hexadiene formation as well as that of oxygen consumption during reduction went through a maximum as the ZnO reduction proceeded. This behavior has been interpreted in terms of two competing effects, i.e., the decrease of surface active oxygen and the increase of propylene adsorption sites, both of which are brought about with increasing the degree of reduction. Such an analysis of reduction behavior may be useful to elucidate interactions between olefins and metal oxide surface

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which are vitally important from mechanistic standpoints. To date the reduction behavior of metal oxide catalysts has been dealt with in a few reports (*2–5*), but the subject has hardly been analyzed sufficiently. In this paper, the reduction behavior of ZnO in a stream of propylene was studied in detail to check the validity of the analysis previously proposed as well as to obtain further information on the catalytic properties of ZnO.

EXPERIMENTAL

Zinc oxide was prepared by thermal decomposition of the zinc hydroxide precipitated from an aqueous solution of zinc nitrate with ammonia, followed by calcination at 600°C for 5 hr. The sample was ground and screened to 40–60 mesh. Surface area as determined by BET method was 1.1 m^2/g. The reduction of ZnO with propylene was carried out in a conventional flow reactor with the same procedure as reported previously (*1*). The amount of oxygen atoms consumed from ZnO was determined from the formation rates of gaseous products.

RESULTS

Time Course of Propylene Reduction of ZnO

As reported previously (*1*), the reduction of ZnO with propylene consumes the oxidic oxygen of ZnO by only a few surface layers. Propylene reacts with the oxygen to form gaseous products: CO_2, benzene (BEN), acetone (ACE), and 1,5-hexadiene (HD). In Fig. 1 the formation rates of gaseous products and the amount of oxygen consumption (Y) are depicted as a function of reduction time (t_r). It is seen that the time courses are largely different depending on the products. As shown in the figure, HD was not formed at $t_r = 0$ but went through a formation maximum as the reduction proceeded. In contrast, the rates for CO_2 and BEN decreased rapidly while that for ACE decreased rather slowly with increasing t_r.

X-Ray diffraction analysis showed no detectable change of ZnO structure after the reduction.

Effects of Contact Time and Water Vapor

It may be possible even under reductive conditions that the partial oxidation products of propylene are oxidized consecutively. This possibility was examined by varying contact time at the initial period of reduction where the oxidic oxygen retains higher activity. As shown in Fig. 2, the conversion of propylene to CO_2 increased rapidly at contact time longer than 0.5 g·s/cm^3, while that to ACE apparently

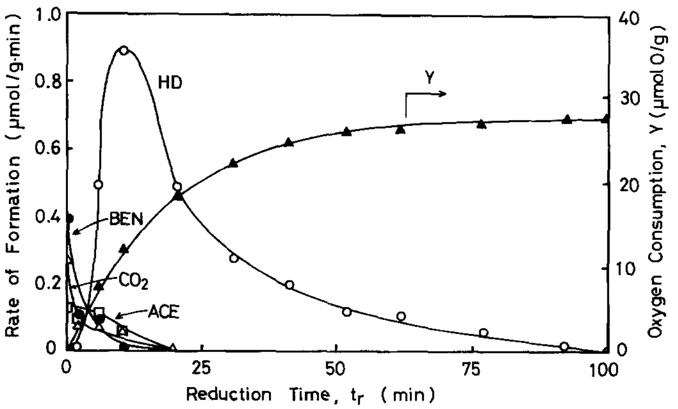

FIG. 1. Time course of the reduction of ZnO with propylene. HD=1,5-hexadiene, BEN=benzene, ACE=acetone. Reaction conditions, temperature (T)=500°C; propylene partial pressure (P_{PR}) = 0.15 atm; contact time (W/F) = 0.5 g·s/cm^3.

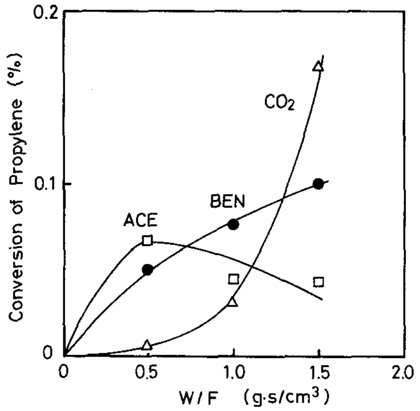

FIG. 2. Effect of contact time (W/F) on the conversion of propylene at $t_r = 0$. $T = 500°C$, $P_{PR} = 0.07$ atm.

reached a maximum at contact time less than 0.5 g·s/cm³. The BEN formation increased monotonously with contact time. These behavior indicates that ACE is easy to be oxidized to CO_2. As such a secondary reaction complicates the kinetic analysis, contact time was fixed to 0.5 g·s/cm³ in the experiments hereafter.

The formation rate of ACE was often scattered in different runs. This scattering might be caused by water vapor contained in the gas stream or in the oxide samples, since water vapor can be a reactant in the catalytic oxidation of propylene to acetone (*6*). The effect of water vapor pressure was examined by adding steam to the gas stream. As a result, the conversion to ACE was almost proportional to the water vapor pressure as shown in Fig. 3, though the formation of CO_2 and BEN was not affected. Small amounts of ACE were still produced even when steam was not fed, for which the surface hydroxyl groups of ZnO as well as the water vapor produced by the propylene oxidation may be responsible. Good reproducibility of the ACE formation was attained by pretreating the ZnO sample with helium at 550°C in the reactor, suggesting that the pretreatment is effective in controlling the surface state of ZnO, especially with respect to the surface hydroxyl groups. The subsequent experiments always adopted this pretreatment.

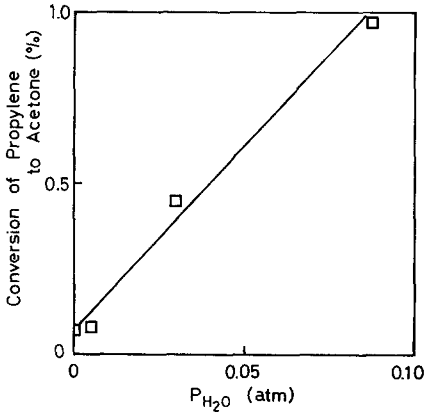

FIG. 3. Effect of water vapor pressure (P_{H_2O}) on the acetone formation. $T = 500°C$, $P_{PR} = 0.07$ atm, $W/F = 0.5$ g·s/cm³.

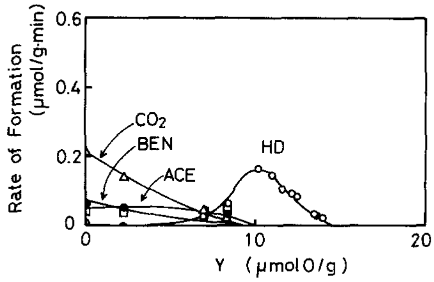

FIG. 4. Changes of the formation rates with oxygen consumption (Y) at $P_{PR} = 0.06$ atm. $T = 500°C$, $W/F = 0.5$ g·s/cm³.

Dependence of Reduction Behavior on Propylene Partial Pressure

In order to reveal the formation behavior of gaseous products from propylene in detail, the propylene partial pressure (P_{PR}) was varied in the range of 0.06 to 0.21 atm. The formation rates of gaseous products at $P_{PR} = 0.06$ and 0.21 atm are respectively shown in Figs. 4 and 5, as functions of the amount of oxygen consumption (Y). The formation behavior of each product remains almost the same irrespective of P_{PR}, though the formation rate itself as well as the total amount of oxygen consumption (Y_∞) is affected by P_{PR}.

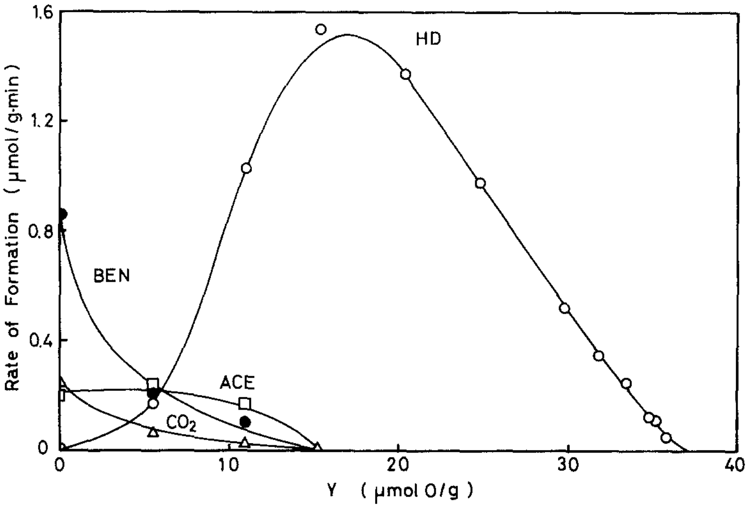

FIG. 5. Changes of the formation rates with oxygen consumption (Y) at $P_{PR} = 0.21$ atm. $T = 500°C$, $W/F = 0.5$ g·s/cm^3.

Figure 6 shows the relation of each formation rate to P_{PR}, where the initial rates at $t_r = 0$ were chosen for BEN, ACE, and CO_2, but for HD the rate at the formation maximum was conveniently used. The pressure dependence is nearly second order for HD and BEN, and first order for ACE. In contrast to these, the CO_2 formation seems to be independent of P_{PR}. The relation between P_{PR} and Y_∞ is shown in Fig. 7. It is clear that Y_∞ becomes larger at higher P_{PR}. This increase of Y_∞ is reflected on the increases of the yields of HD, BEN, and ACE. However, the CO_2 formation was not affected by P_{PR}.

It should be added that the duration of reduction remained almost the same irrespective of P_{PR}; CO_2, BEN, and ACE ceased to form at ca. 20 min, respectively, and the HD formation ceased at ca. 100 min.

DISCUSSION

Property of Available Oxygen

As mentioned above, ZnO can be reduced partially with propylene. The reduction reaction is expressed as

$$ZnO + pC_3H_6 \rightarrow Zn + q \quad \text{(oxidation products)} \qquad (1)$$

where p and q denote stoichiometric coefficients. The standard free energy changes of Eq. (1) at 500°C are 10, 12, 21, and 27 kcal for BEN, CO_2, ACE, and HD formation (*7*, *8*), respectively, indicating that the reactions are thermodynamically unfavorable under the conditions. Therefore, the oxygen actually eliminated during the reduction should be in a higher energy state

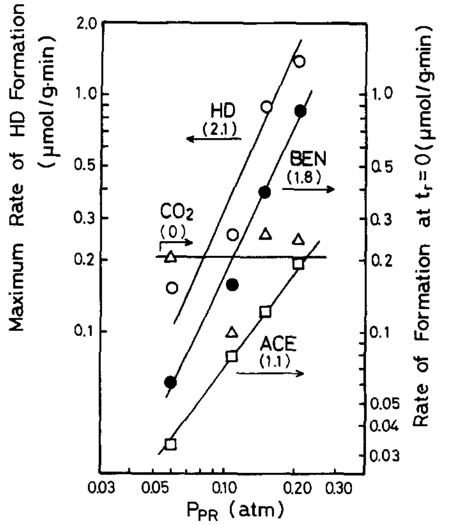

FIG. 6. Dependence of the formation rates on the propylene partial pressure (P_{PR}). The figures in parentheses represent slopes.

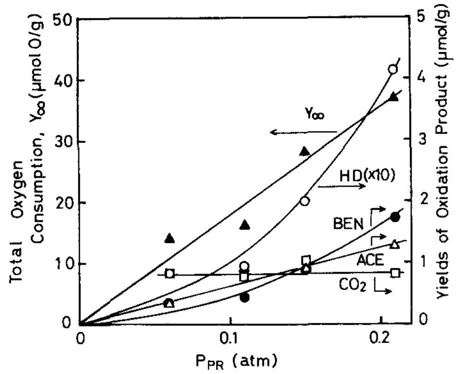

FIG. 7. Dependences of the amount of total oxygen consumption and the yields of oxidation products on the propylene partial pressure (P_{PR}).

than the normal lattice oxygen, i.e., adsorbed oxygen and/or the lattice oxygen associated with some sort of lattice defects. As seen in Fig. 7, total oxygen consumption (Y_∞) increases with a rise in P_{PR}. This fact probably means that the oxygen consumption causes the nonstoichiometry of ZnO and that the nonstoichiometry becomes larger at higher chemical potential of propylene, although the nonstoichiometry of ZnO has been reported to be very small under usual conditions (*9*). Taking a closer look, however, there is a distinction in formation behavior between CO_2 and the other gaseous products. That is, the rate and total amount of CO_2 formation, are almost independent of P_{PR} (Figs. 6 and 7), while those of BEN, ACE, and HD depend sensitively on P_{PR}. This fact suggests that the oxygen species leading to CO_2 is different from those to the other products. We consider that the initial ZnO surface contains a small amount of highly reactive oxygen (probably adsorbed oxygen) which is responsible for the CO_2 formation, and that the lattice oxygen associated with the nonstoichiometry leads to the other products. With this difference of oxygen species in mind, the formation behavior of the partial oxidation products was analyzed after the correction of the oxygen consumption due to the CO_2 formation.

Analysis of 1,5-Hexadiene Formation

We focus attention on the 1,5-hexadiene formation which showed very interesting behavior; the rate is zero at first but goes through a large maximum with the progress of reduction. Figure 8 depicts formation curves for HD at different propylene pressures (P_{PR}) as a function of the amount of oxygen consumed (Y'), from which the oxygen consumed for the CO_2 formation has been excluded on the reason described before. Very important is the fact that, though the rate and Y'_∞ increase together with increasing P_{PR}, the data at different P_{PR} are fit well to the analytical curves of the same form

$$R_{HD} = k(Y')^2(Y'_\infty - Y')^2 \qquad (2)$$

as shown in the figure. Here R_{HD} is the rate of HD formation, and k is a constant which depends on P_{PR} and temperature. If we use Y instead of Y', no such simple analytical curves can be obtained. This again supports the assumption that different oxygen species are consumed for CO_2 and the other products.

What is the implication of the rate Eq. (2)? In the previous paper (*1*), we explained the occurrence of the rate maximum in the HD formation by combining two effects, i.e., a rate-increasing effect, and a rate-decreasing effect. The latter apparently comes from a decrease in reactive oxygen concentration at the surface. The former was proposed to arise from an increase of the adsorption sites for propylene, which were ascribed to the surface zinc atoms uncovered or coordinatively unsaturated after the removal of surface oxygen. The concentrations of surface active oxygen (excluding the oxygen used for the CO_2 formation) and of the exposed zinc atoms are assumed to be proportional to $(Y'_\infty - Y')/Y'_\infty$ and Y'/Y'_∞, respectively. Assuming a Langmuir type adsorption for propylene on the exposed zinc atoms, the rate of surface reaction between

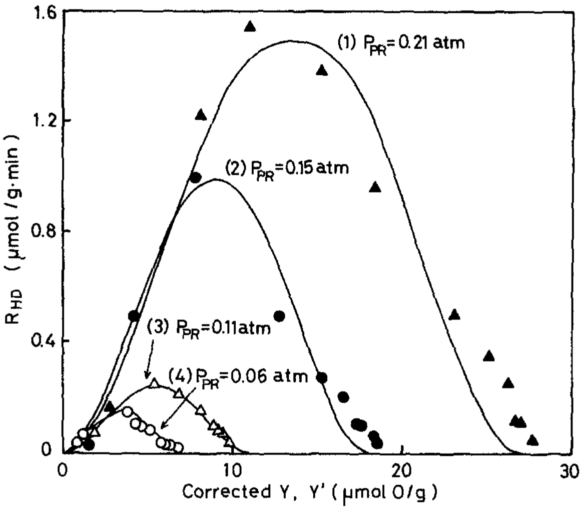

FIG. 8. Analysis of the rates of HD formation (R_{HD}) at various P_{PR}. Solid lines show analytical curves for R_{HD} (μmol/g·min), (1) $4.7 \times 10^{-5}(Y')^2(27 - Y')^2$; (2) $1.5 \times 10^{-4}(Y')^2(18 - Y')^2$; (3) $2.6 \times 10^{-4}(Y')^2(11 - Y')^2$; (4) $1.0 \times 10^{-3}(Y')^2(7 - Y')^2$.

the adsorbed propylene and the reactive oxygen is given as follows (*1*).

$$R_{HD} = k'(1/Y'_\infty)^{m+n}[KP_{PR}/(1 + KP_{PR})]^m \times (Y')^m(Y'_\infty - Y')^n \quad (3)$$

where m and n are the reaction orders on P_{PR} and reactive oxygen, respectively, K is the equilibrium constant of propylene adsorption, and k' is an apparent rate constant. For a constant P_{PR}, Eq. (3) is rewritten as Eq. (4).

$$R_{HD} = k(Y')^m(Y'_\infty - Y')^n \quad (4)$$

With $m = 2$ and $n = 2$, Eq. (4) is identical with Eq. (2). According to this analysis, moreover, R_{HD} should depend on P_{PR} with second order, assumining $1 \gg KP_{PR}$ in Eq. (3). The second order dependence was obtained experimentally as shown in Fig. 6. This agreement, i.e., $m = 2$, assures the validity of the foregoing analysis.

The result $m = 2$ suggests that the HD formation requires two propylene adsorption sites, i.e., either two exposed zinc atoms or two coordinatively unsaturated sites on one zinc atom. Similarly $n = 2$ indicates that two oxidic oxygen atoms are required in the rate-determining steps; each oxygen atom is probably used to abstract an allylic hydrogen atom from adsorbed propylene. This scheme is consistent with the earlier proposal based on kinetic studies under the catalytic oxidation conditions (*10*). It appears that reduction study such as this can provide more detailed information on the surface interaction than the usual kinetic studies do.

Behavior of Acetone and Benzene Formation

The formation behavior of ACE and of BEN is less clear since they were formed only at earlier stages of reduction and in quantities far smaller than HD. The fact that their formation occurred from the onset of reduction indicates that the original ZnO surface possesses a limited number of sites favorable for their formation. The BEN formation at $t_r = 0$ depended on P_{PR} in second order, suggesting that the rate-determining step includes a coupling of propylene. As the reduction proceeded, its rate decreased monotonously unlike that of another dimerized product HD. This may reflect that more oxygen atoms are required for the BEN formation than for the HD formation. These suggest that the original ZnO surface contains some uncovered zinc atoms surrounded by oxygen atoms sufficient to convert a couple of propylene molecules to BEN. As the surface oxygen is depleted, the oxygen atoms surrounding such sites become insufficient to form BEN but still sufficient to form HD. At the same time, the oxygen depletion from the surface uncovers zinc atoms, resulting in creation of new sites for HD formation as proposed in the foregoing section. These features of HD and BEN formation well explain the fact that the rate for HD + BEN does not change monotonously but possesses a minimum as can be concluded from Figs. 4 and 5. As for the ACE formation, the observed promoting effect of water vapor supports that water molecules participate in the reaction as considered in the catalytic propylene oxidation (*6*), but the analysis of its formation behavior is difficult at present.

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