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Oxidative Dehydroaromatization

II. Oxidation of Propylene Over Binary Oxide Catalysts Containing Bismuth or Tin

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Catalytic properties of various metal phosphates and binary oxides containing bismuth or tin for the oxidation of propylene have been studied at 300-600°C. The active catalysts are divided into two groups: one has high selectivity for benzene formation (oxidative dehydroaromatization), and another is effective for acrolein formation. Bismuth salt catalysts, such as phosphate, arsenate, basic sulfate, and titanate, belong to the former; whereas bismuth molybdate belongs to the latter. In the case of stannic oxide, benzene formation is highly enhanced by addition of basic oxides; whereas acrolein formation is promoted by acidic oxides.

These facts indicate that Bi^{3+} and Sn^{4+} ions provide the adsorption sites for the allylic intermediate under the influence of adjacent $M^{n+}-O^{2-}$ groups, and that the course of reaction depends on the acid-base properties of the adsorption sites. The acid-base properties are considered to influence the nature of the adsorbed allylic species (radical- or cation-like). Selectivity of reaction is discussed from this point of view.

INTRODUCTION

In a recent letter to the Editors (*1*), we have reported that aromatic hydrocarbons are formed in the oxidation of lower olefins over bismuth phosphate catalysts. This aromatization was also reported over binary oxides containing bismuth by Ohdan *et al.* (*2*), independently. The reaction was considered to proceed through several consecutive steps in the presence of oxygen (*1*): the oxidative dehydrogenation of olefins to allylic intermediates, the dimerization of the allylic intermediates to diolefins such as 1,5-hexadiene, and the aromatization of the dimerized diolefins. The mechanism of this reaction via an allylic intermediate has been confirmed by the comparison of products from butene isomers. Thus, the reaction can be designated as oxidative dehydroaromatization, which can appropriately be classified as one of the allylic oxidations of olefins (*3*). The reaction is clearly distinguished from the well-known dehydrocyclizations of C_6 and higher paraffins or olefins, and from the dehydrocyclodimerization of C_3–C_5 paraffins or olefins, which was reported by Csicsery (*4*).

In the present work, the oxidation of propylene to benzene or acrolein was investigated by using various metal phosphate catalysts and binary oxide catalysts containing bismuth or tin, to identify the active catalysts for the oxidative dehydroaromatization. It is also of interest to identify those properties of catalysts that determine their selectivities for two types of allylic oxidations, namely, whether propylene will be converted to benzene by the coupling of two allylic intermediates, or to acrolein by the addition of oxygen.

EXPERIMENTAL METHODS

Catalysts

Eight kinds of metal phosphates, Ca^{2+}, Cr^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Ce^{3+}, were used. Calcium and nickel phosphates were of commercial origin. Other phosphates were prepared by evaporation to dryness of the diammonium hydrogen phosphate solution including the metal nitrate or oxide, followed by calcination.

Two types of binary oxide catalysts containing bismuth were used. The first type was the bismuth salts of oxy acids. They were prepared from a mixture of bismuth nitrate solutions and the ammonium salt of oxy acid, by the evaporation–calcination method. However, basic bismuth sulfate, $(BiO)_2SO_4$, was obtained by thermal decomposition of commercial bismuth sulfate, $Bi_2(SO_4)_3$, at 600°C. The other type of catalyst was the bismuth oxide–metal oxide system, which was prepared by heating the mixture of two oxides of commercial origin.

Stannic oxide was prepared by calcination of stannic acid precipitated from stannic chloride solution with ammonia. Binary oxide catalysts containing stannic oxide were prepared by impregnation of stannic oxide with alkali or alkaline earth hydroxide solution, or with the ammonium salt of oxy acid solution.

All catalysts were calcined at 600°C for 5 hr. Granules of 48–80 mesh were used.

Apparatus and Procedures

The oxidation reaction was carried out in a flow system at atmospheric pressure, using an 8-mm i.d. Pyrex or quartz glass tube reactor with a fixed catalyst bed. The typical composition of feed gas was 9% propylene, 18% oxygen, and 73% nitrogen. The feed gas was passed at a contact time $W/F = 0.5$ or 2.0 g sec/ml, over the catalyst in the temperature range of 300–600°C. The reaction temperature was measured by a thermocouple placed in the catalyst bed. Under these conditions, a steady state was attained within 1 hr, and this was held for 5 or 10 hr. The formation of coke was not observed. The feed and exit gases were analyzed by gas chromatography, using Porapak Q for propylene and carbon dioxide, and 10% PEG 6000 on Cerite 545 for acrolein and benzene.

RESULTS

Metal Phosphate Catalysts

The catalytic activities and selectivities of eight metal phosphates and three typical bismuth phosphates at 500°C are shown in Table 1. X-Ray diffraction at room temperature showed that all catalysts were orthophosphates, except that with Bi/P = 2, which was a mixture of $\gamma\text{-}Bi_2O_3$, $3Bi_2O_3\cdot P_2O_5$, $2Bi_2O_3\cdot P_2O_5$, and three forms of $BiPO_4$ (hexagonal, high temperature, and monazite).

TABLE 1

OXIDATION OF PROPYLENE OVER METAL PHOSPHATE CATALYSTS

$C_3H_6 = 9\%$; $O_2 = 18\%$; $T = 500°C$; $W/F = 2.0$ g sec/ml.

Catalysts	Conversion of propylene (%) to: CO_2	C_3H_4O	C_6H_6
$Ca_3(PO_4)_2$	17.1	0	0
$CrPO_4$	5.2	0	0
$FePO_4$	31.3	8.5	0
$Co_3(PO_4)_2$	4.8	0	0
$Ni_3(PO_4)_2$	1.7	0.2	0
$Cu_3(PO_4)_2$	39.6	5.1	0
$Zn_3(PO_4)_2$	4.6	0.2	0
$CePO_4$	2.5	0.4	0
$BiPO_4$ (high temp type)	51.0	5.7	23.1
(monazite type)	19.3	19.2	4.5
$2Bi_2O_3\cdot P_2O_5$ (Bi/P = 2)	45.0	0	35.4

Among the phosphates examined, only three bismuth phosphates showed activities for benzene formation, although $FePO_4$ and $Cu_3(PO_4)_2$ yielded a small amount of acrolein. Therefore, it may be said that the presence of phosphate ion is not a sufficient requirement for the oxidative dehydroaromatization, but that Bi^{3+} ion is essential. Incidentally, and contrary to normal expectations, it was found that $Ca_3(PO_4)_2$ showed considerable activity for CO_2 formation.

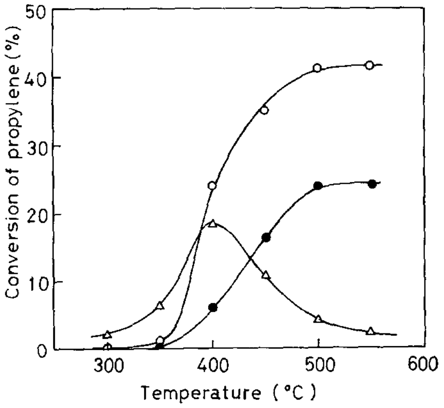

FIG. 1. Oxidation of propylene over $BiAsO_4$ catalyst: $C_3H_6 = 9\%$; $O_2 = 18\%$, $W/F = 2.0$ g sec/ml; —○—, conversion of propylene to carbon dioxide; —●—, to benzene; —△—, to acrolein.

Catalysts of Bismuth Salts of Oxy Acids

The catalytic action of Bi^{3+} was examined in detail by the use of bismuth arsenate, basic bismuth sulfate, and bismuth molybdate catalysts. The temperature dependence of product formation over bismuth arsenate and basic bismuth sulfate is shown in Figs. 1 and 2, respectively. Both the formation of acrolein and of benzene were observed over these catalysts: acrolein at 300–450°, and benzene at 400–550°. The Bi_2O_3–MoO_3 system, which is the most effective catalyst for acrolein formation, has also the structure of an oxy salt (*5*). But this system was inactive for benzene formation, even at the higher temperatures, as shown in Table 2.

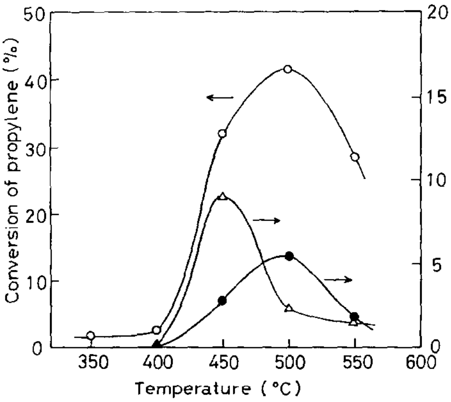

FIG. 2. Oxidation of propylene over $(BiO)_2SO_4$ catalyst: $C_3H_6 = 9\%$; $O_2 = 18\%$; $W/F = 2.0$ g sec/ml; —○—, conversion of propylene to carbon dioxide; —●—, to benzene; —△—, to acrolein.

TABLE 2

OXIDATION OF PROPYLENE OVER BISMUTH MOLYBDATE CATALYSTS

$C_3H_6 = 9\%$; $O_2 = 18\%$; $T = 500°C$; $W/F = 2.0$ g sec/ml.

	Conversion of propylene (%) to:		
Catalysts	CO_2	C_3H_4O	C_6H_6
$(BiO)_2MoO_4$ (Bi/Mo = 2)	12.8	24.9	0
$Bi(BiO)(MoO_4)_2$ (Bi/Mo = 1)	2.9	20.8	0
$Bi_2(MoO_4)_3$ (Bi/Mo = 2:3)	0.3	5.6	0

Thus, bismuth salt catalysts proved to be active for the allylic oxidation. But for selectivity, the influence of oxy anions, or M^{n+}–O^{2-} groups adjacent to Bi^{3+}, must be noted in addition to the role of Bi^{3+}. These effects, and the temperature effect, are discussed below.

Catalysts of Bismuth Oxide–Metal Oxide System

The specificity of Bi^{3+} ion was further confirmed by testing the activities of the bismuth oxide–metal oxide system at the atomic ratio Bi/M = 1. Results at 500 and 550°C are shown in Table 3. Many other binary oxide systems were also found to be effective for the oxidative dehydroaromatization. In particular, the activity of Bi_2O_3–TiO_2 was comparable with those of the bismuth phosphate catalyst systems. X-Ray diffraction of the Bi_2O_3–TiO_2 system at room temperature showed that this catalyst was composed of bismuth titanate, $Bi_4(TiO_4)_3$, and small amounts of Bi_2O_3 and of TiO_2. However, certain other systems were found to be merely mixtures of two oxide components. This observation suggests that the active surface compounds may be formed in the working state in these latter systems.

Stannic Oxide Catalysts Promoted by Basic or Acidic Oxides

These catalysts were also found to be active for the allylic oxidations of propylene. Their high activities were found to

TABLE 3

OXIDATION OF PROPYLENE OVER CATALYSTS OF BISMUTH OXIDE–METAL OXIDE SYSTEMS

C_3H_6 = 9%; O_2 = 18%; W/F = 2.0 g sec/ml.

Reaction temp:	500°C			550°C		
	Conversion of propylene (%) to:			Conversion of propylene (%) to:		
Catalysts (Bi/M = 1)	CO_2	C_3H_4O	C_6H_6	CO_2	C_3H_4O	C_6H_6
$Bi_2O_3 + TiO_2$	45.7	0.2	10.1	57.3	0.8	23.8
$+ NiO$	36.2	0.1	1.8	57.4	0.1	3.7
$+ Sb_2O_4$	6.4	0.4	0.2	11.7	0.6	1.5
$+ SiO_2$	8.4	0.1	0	18.7	0.4	0.8
$+ Fe_2O_3$	11.2	0	0	25.4	0.2	0.6
$+ Al_2O_3$	2.8	0.1	0	11.1	0.8	0
$+ CdO$	2.3	0	0	2.6	0	0

come from the promoting effects of basic or acidic oxides, as follows.

Figure 3 shows the promoting effects of basic Na_2O and acidic P_2O_5 on the selectivity of stannic oxide. Addition of Na_2O greatly enhanced benzene formation, while addition of P_2O_5 resulted in increase of acrolein formation, although total activity decreased. Other basic and acidic oxides also showed similar promoting effects, except for alkaline earth oxides, as shown in Table 4. In Table 4, only the results at 550°C are listed, but analogous results were obtained at the higher temperatures.

DISCUSSION

Two types of binary oxide catalysts were found to be active for allylic oxidations of propylene to benzene and acrolein. One was a catalyst containing bismuth, such as Bi_2O_3–P_2O_5, –As_2O_5, and –TiO_2. Another catalyst was the stannic oxide promoted by a basic or an acidic oxide.

Catalytic activities of the first named group arise from formation of a bismuth salt of an oxy acid, that is to say between Bi_2O_3 and the second oxide, neither of which is active if used alone. In this system, it is reasonable to accept that Bi^{3+}

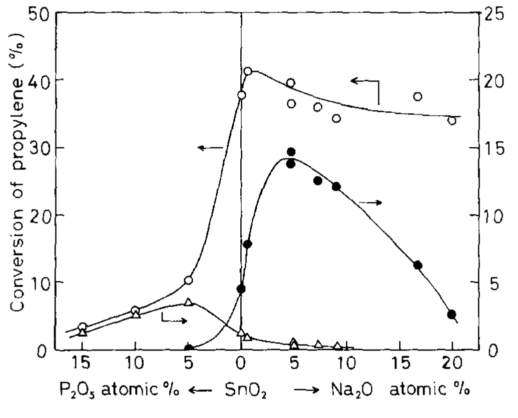

FIG. 3. The promoting effects of Na_2O and P_2O_5 on the catalytic behavior of stannic oxide: C_3H_6 = 12%; O_2 = 24%; W/F = 0.5 g sec/ml; T = 550°. —○—, conversion of propylene to carbon dioxide; —●—, to benzene; —△—, to acrolein.

TABLE 4

THE PROMOTING EFFECTS OF BASIC AND ACIDIC OXIDES ON THE CATALYTIC PROPERTIES OF STANNIC OXIDE

C_3H_6 = 9%; O_2 = 18%; T = 550°C; W/F = 0.5 g sec/ml.

Catalysts[a] (Sn/M = 20:1)	Conversion of propylene (%) to:		
	CO_2	C_3H_4O	C_6H_6
SnO_2	37.7	1.2	4.5
$SnO_2 + Li_2O$	40.2	Tr	7.0
$+ Na_2O$	36.6	0.4	14.7
$+ K_2O$	36.3	0	5.1
$+ MgO$	38.3	0.4	1.6
$+ CaO$	40.2	0	4.7
$+ BaO$	41.6	0	Tr
$+ P_2O_5$	10.3	3.5	Tr
$+ As_2O_5$	39.9	3.0	Tr
$+ Sb_2O_4$	34.1	2.0	1.8
$+ MoO_3$	33.0	8.7	Tr
$+ WO_3$	40.4	2.0	Tr

[a] Acid strength of pure SnO_2 was in the range of $+3.3 \sim +1.5$. All the samples promoted by basic or acidic oxides had the value of $+12.2$ $+9.3$ or of $+1.5 \sim -3.0$. As to Hammett's indicators used, see footnote *a* of Table 5.

ions acquire activity for allylic oxidation owing to the influence of adjacent oxy anions or M^{n+}–O^{2-} groups. Therefore, Bi^{3+} ions combined to other metal ions through O^{2-} ions may be considered to act as the adsorption sites for the allylic intermediate. Batist *et al.* (*6*) and Peacock *et al.* (*7*) assumed that the adsorption sites for the allylic intermediate over bismuth molybdate catalysts would be Mo^{6+} ions. However, over this catalyst, it is more appropriate to suppose that Bi^{3+} ions provide the active site under the influence of adjacent oxy anion MoO_4^{2-}, as in the case of other oxy salts.

On the other hand, stannic oxide is more or less active for two allylic oxidations. This fact shows that Sn^{4+} appears to be the active component, or the adsorption site for the allylic intermediate, although its selectivity for benzene or acrolein is highly promoted by the addition of basic or acidic oxides, respectively.

The factors that control the selectivity for benzene or acrolein constitute a more complex problem. Though a quantitative discussion of selectivity cannot be made completely (since conversion levels were quite different), two factors on selectivity are indicated; the temperature, and the acid–base properties of the catalysts.

Temperature affects selectivity as shown in Figs. 1 and 2, which show that selectivity changes from primarily acrolein to primarily benzene by a temperature change by about 50°C. A full understanding of this effect requires information concerning the rate-determining steps in both oxidations. However, since the only difference between the two reactions is whether an allylic intermediate will be attacked by another allylic intermediate or by a surface oxygen anion, the temperature rise may be considered to result in the acceleration of the former coupling process between two intermediates. This possibly occurs by increasing the lability of the allylic species more than that of oxygen anions.

However, a catalyst capable of forming acrolein at the lower temperature does not always become capable of forming benzene by a mere increase of temperature. Thus, a distinction between catalysts as being benzene-forming and acrolein-forming was made from the selectivity values at the constant temperature of 500 or 550°. In the case of stannic oxide catalysts, benzene formation was highly enhanced by the addition of basic oxides, while that of acrolein was enhanced by acidic oxides. This fact suggests that for these reactions, as is well known for many other catalysts, acid–base properties and reactions play an important role in their catalytic behavior. A similar relationship between selectivity and acid–base properties was observed in the case of various bismuth salt catalysts as shown in Table 5, in which selectivities at 500° and acid strength measured using Hammett's indicators (*8*) are listed. Less acidic catalysts such as that with Bi/P = 2 are ben-

TABLE 5

SELECTIVITY FOR THE ALLYLIC OXIDATIONS OF PROPYLENE AND ACID STRENGTH OF BISMUTH SALT CATALYSTS

C_3H_6 = 9%; O_2 = 18%; T = 500°C; W/F = 1.0 g sec/ml.

Catalysts	Selectivity (%) for: C_6H_6	C_3H_4O	Acid strength[a] H_0
$2Bi_2O_3 \cdot P_2O_5$ (Bi/P = 2)	49.0	0	+7.1 ~ +6.8
$BiAsO_4$ (monazite form)	33.8	5.8	+6.8 ~ +4.0
$BiPO_4$ (high temp form)	26.9	6.6	+6.8 ~ +4.0
$Bi_2O_3 \cdot 2TiO_2$ (Bi/Ti = 1)	18.0	0.3	+7.1 ~ +6.8
$(BiO)_2SO_4$	10.1	4.0	+6.8 ~ +4.0
$BiPO_4$ (monazite form)	9.1	38.6	+1.5 ~ −3.0
$(BiO)_2MoO_4$ (Bi/Mo = 2)	0	66.1	+3.3 ~ +1.5
$Bi(BiO)(MoO_4)_2$ (Bi/Mo = 1)	0	91.7	+1.5 ~ −3.0
$Bi_2(MoO_4)_3$ (Bi/Mo = 2/3)	0	94.9	+1.5 ~ −3.0

[a] Hammett's indicators used were 2,4,6-trinitroamine (pK_{BH} = +12.2), phenolphthalein (+9.3); bromothymol blue (+7.1); neutral red (+6.8); phenylazonaphthylamine (+4.0); butter yellow (+3.3); benzeneazodiphenylamine (+1.5); and dicinnamalacetone (−3.0).

zene-forming while more acidic ones such as bismuth molybdate are acrolein-forming. It might be thought that the reverse effects would be observed for acidic P_2O_5 on SnO_2 and on Bi_2O_3, but this view is easily dispelled by the fact that Bi_2O_3 is more basic than SnO_2. The acid strength of SnO_2 modified by P_2O_5 was in the range of $H_0 = +1.5 \sim -3.0$.

Acidity of the metal oxide can be considered to influence the course of the reaction two ways. It may alter the electronic properties of the adsorbed allylic intermediate, or, it may affect the metal-oxygen bond strength. But, selectivity for benzene or acrolein formation may be explained qualitatively in terms of the electronic state of the allylic intermediates as below.

In allylic oxidation, an allylic intermediate has been indicated to be neutral or slightly positive (*9*). Its electronic structure may depend on the acid-base properties of the adsorption site, Bi^{3+} or on Sn^{4+}. On acidic sites, because of the large electronegativity of the metal ion, the electron of the allylic species would be localized to a metal ion. Then the intermediate would become cationic and so susceptible to nucleophilic addition of oxygen anion. Thus, the more acidic is the catalyst, the higher becomes its selectivity for acrolein formation. On the other hand, on less acidic site the allylic species would hold its radical-like character. It is more reasonable that benzene would be formed from the radical-like species, since little electrostatic repulsion in the dimerization step of two allylic intermediates would occur.

The promoting effects of oxy anions on Bi^{3+} ions, and of basic or acidic oxides on SnO_2, are, based on the principle of electronegativity equalization, probably those which induce the changes in the electronic state or the acid-base properties of the adsorption sites through the bond of Bi^{3+} (or Sn^{4+})-O^{2-}-M^{n+}. If M^{n+} is more electronegative than Bi^{3+} or Sn^{4+}, and if the ratio of M^{n+}/Bi^{3+} (or Sn^{4+}) is large, the adsorption site becomes more acidic, and vice versa.

The selectivities of these catalysts may be explained qualitatively as above. Nevertheless, the acid-base properties are not always the sole factor deciding the catalytic behaviors. Other properties, such as the oxidation-reduction properties, the electronic state, and the mobility of O^{2-} ions on the surface, and the susceptibility of the metal ion to combine with the allylic species, must be also taken into account to explain why only Bi^{3+} and Sn^{4+} are so effective. But these effects remain to be proved, in particular for the mixed oxide catalysts.

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