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LETTER TO THE EDITORS

New Catalytic Aromatization of Lower Olefins over Bismuth Phosphate Catalyst

The catalytic oxidation of propylene to acrolein and of *n*-butenes to butadiene over such mixed oxide catalysts as Bi–Mo oxides, Bi–Mo–P oxides, Sn–Sb oxides, and Cu–Se oxides, is well known (*1*). In the present investigation, new catalytic aromatization of propylene was found over bismuth phosphate, bismuth arsenate, bismuth antimonate, and Bi_2O_3–SnO_2 catalysts. So some reaction conditions for aromatization were investigated. Voge and Adams (*2*) reported the oxidative dehydrogenation of 1-butene to butadiene over bismuth phosphate catalyst, however could not observe any aromatics.

Bismuth phosphate catalysts were precipitated from diammonium hydrogenphosphate [$(NH_4)_2HPO_4$] and bismuth nitrate [$Bi(NO_3)_3 \cdot 5H_2O$] in an acidified aqueous solution. After drying at 120°C, the catalysts were calcined at 500°C for 5 hr in the atmosphere. The oxidation reactions were carried out in a flow system at atmospheric pressure using a Pyrex glass reactor with a fixed catalyst bed. The reaction products were identified by mass spectroscopy, IR and UV, and analyzed by gas chromatography.

In the oxidation of propylene over bismuth phosphate catalysts, carbon dioxide, acrolein and benzene were the main products, with small amounts of carbon monoxide, acetaldehyde, and 1,5-hexadiene. Figure 1 shows the dependence of the product distribution upon the atomic ratio of bismuth/phosphorus (Bi/P). The formation of benzene was maximal at Bi/P = 2. Its selectivity was about 40%. At Bi/P = 1, acrolein was formed in a considerable amount. By X-ray diffraction analysis, the latter catalyst (Bi/P = 1) was found to be monazite type or high temperature type $BiPO_4$, and the former was the mixture of hexagonal $BiPO_4$, monazite type $BiPO_4$, high temperature type $BiPO_4$, $2Bi_2O_3 \cdot P_2O_5$, and γ-BiO_3. Phosphorus was found to exist as PO_4^{3-} by IR. The active species for acrolein, benzene, and carbon dioxide may be monazite type or high temperature type $BiPO_4$, hexagonal $BiPO_4$ or $2Bi_2O_3 \cdot P_2O_5$, and γ-Bi_2O_3, respectively.

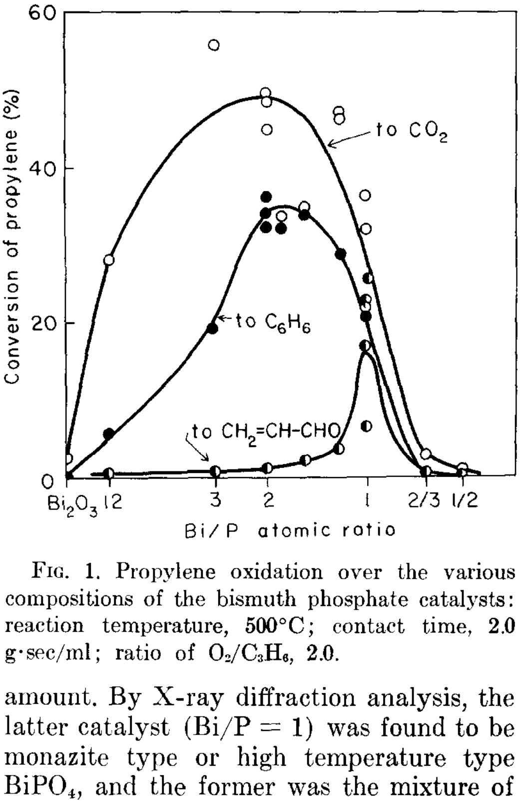


FIG. 1. Propylene oxidation over the various compositions of the bismuth phosphate catalysts: reaction temperature, 500°C; contact time, 2.0 g·sec/ml; ratio of O_2/C_3H_6, 2.0.

The optimum conditions for the benzene formation from propylene over the Bi/P = 2 catalyst were the temperature of 500°C, the contact time of 1–2 g·sec/ml and the

TABLE 1

THE EFFECTS OF SOME REACTION CONDITIONS ON THE OXIDATION OF PROPYLENE OVER THE Bi/P = 2 CATALYST

Reaction temp (°C)	Contact time (g · sec/ml)	Ratio of O_2/C_3H_6	Conversion of propylene (%) Total	To CO_2	To benzene	Selectivity for benzene (%)
350	2.0	1.6	9.8	9.1	0.7	7.2
400	2.0	1.6	26.8	23.9	2.9	10.8
450	2.0	1.6	83.0	50.8	28.6	34.5
500	2.0	1.6	87.6	49.2	34.3	39.2
	3.0	1.6	88.3	49.9	34.6	38.9
	1.0	1.6	85.8	43.3	38.6	44.9
	0.5	1.6	55.0	27.8	22.7	41.2
	0.3	1.2	30.5	15.1	12.5	41.2
	2.0	0.72	49.6	23.9	23.1	46.5
	1.0	0.60	39.4	19.9	17.2	43.8
	1.0	0.40	26.7	13.9	11.3	42.0

oxygen to propylene ratio of unity, as shown in Table 1.

The results for butene isomers over the Bi/P = 2 catalyst are summarized in Table 2. As expected, aromatic products were observed, although their selectivities were lower and their sorts were complex. The main products of partial oxidation were 2,5-dimethyl-1,5-hexadiene and *p*-xylene from isobutene, however, it was 1,3-butadiene from *n*-butenes.

The aromatization reaction of propylene

TABLE 2

OXIDATION OF BUTENE ISOMERS OVER THE Bi/P = 2 CATALYST

Reaction temp, 550°C; contact time, 0.37 g · sec/ml.

	Isobutene	1-Butene	*cis*-2-Butene	*trans*-2-Butene
Feed gas (%)				
Olefin	13.7	12.3	13.7	11.8
Air	86.3	87.7	86.3	88.2
Conversion (%)				
Olefin	48.2	28.6	29.4	21.3
O_2	88.3	75.3	67.2	56.2
Selectivity (%)				
$CO_2 + CO$	43.2	62.1	62.3	61.0
1,3-Butadiene	—	27.3	28.2	27.2
Dimers (C_8H_{14})	29.4[a]	4.9[b]	3.4[b]	3.5[b]
Aromatics	28.6	4.9	2.5	2.5
Benzene	2.5	1.4	0.7	0.7
Toluene	8.0	1.5	0.9	0.7
p-Xylene	11.3	0.5	0.2	0.2
m-Xylene	4.4	0.2	0.1	0.1
o-Xylene	1.6	0.5	0.2	0.3
Ethyl benzene	—	0.2	0.1	0.1
Styrene	—	0.6	0.3	0.5

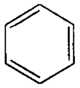
[a] 2,5-Dimethyl-1,5-hexadiene, 20.9%; 2,5-dimethyl-2,4-hexadiene, 8.5%.

[b] The structures of dimers from *n*-butenes were not determined yet.

may be supposed to proceed as following:

$$2CH_2{=}CH{-}CH_3 \xrightarrow{-2H}$$

$$2CH_2{\doteq}CH{\doteq}CH_2 \xrightarrow{-4H}$$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where $CH_2{\doteq}CH{\doteq}CH_2$ is a π-allyl intermediate. This mechanism is supported by the simultaneous formation of the products via a π-allyl intermediate such as acrolein (*1*). 1,5-Hexadiene and 2,5-dimethyl-1,5-hexadiene can be also explained to be formed via a π-allyl intermediate.

Batist *et al.* (*3*) postulated that Mo^{6+} ion was the active site for the formation of a π-allyl intermediate, whereas Bi^{3+} ion was only the promoter of the dehydroxylation of surface OH^- groups formed by the abstraction of a hydrogen atom from the olefin. However, in our experiment, the binary bismuth oxide catalysts such as bismuth phosphate, bismuth arsenate, bismuth antimonate, and Bi_2O_3–SnO_2 had catalytic activities for acrolein and benzene, although other metal phosphates than bismuth such as cobalt(II), antimony(III) and nickel(II), had no activity. This fact suggests that Bi^{3+} ion plays an important role for the π-allyl intermediate formation in this catalysis. More precise investigations on the reaction mechanism are in progress.

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