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The Effect of Bismuth Addition to the Molybdenum–Phosphorus Oxide Catalyst on the Partial Oxidation of Butene, Butadiene, and Furan

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The vapor-phase air oxidation of *cis*-2-butene, butadiene, furan, and maleic anhydride was carried out over various Mo–Bi–P oxide catalysts with different Bi/Mo ratios (P/Mo = 0.2 atomic ratio) at the concentration of about 0.66%, in order to elucidate the effect of the Bi_2O_3 addition to the MoO_3–P_2O_5 catalyst on the activity and selectivity for the oxidation of each reactant. The oxidation activity for butene, butadiene, and furan increases with an increase in Bi_2O_3 content and goes through a maximum at Bi/Mo = 0.10. With a further increase in Bi_2O_3, it decreases. However, the activity for maleic anhydride sharply increases with Bi_2O_3 content. We attempted to explain the result by using the acid–base nature of reactant and catalyst. The highest yields of maleic anhydride are obtained at Bi/Mo = 0.1 in the oxidations of butene, butadiene, and furan, and reach 30, 60, and 76 mole %, respectively, based on the reactants fed in. When Bi/Mo is over 0.1, the yields decrease remarkably. This is attributable to the fact that the activity for the secondary oxidation of maleic anhydride grows to a significant extent, thus no longer being negligible.

INTRODUCTION

The catalytic partial oxidation of the C_4 fraction of petroleum hydrocarbons to maleic anhydride (MA) is very attractive from both the scientific and industrial points of view. There are numerous patents dealing with the oxidation, but the volume of the nonpatent literature is still scanty (*1, 2*). On the basis of detailed kinetic studies on the mechanism of the oxidation of butene to maleic anhydride over V_2O_5, V_2O_5–P_2O_5, and V_2O_5–MoO_3 catalyst systems, we have proposed, as the main reaction pathway, the following consecutive steps: $C_4H_8 \rightarrow C_4H_8\text{ ads} \rightarrow C_4H_6\text{ ads} \rightarrow C_4H_4O\text{ ads} \rightarrow \text{MA}$, and have discussed the effect of such additives to V_2O_5 as P_2O_5 and MoO_3 on the rate and selectivity of the reaction (*3–8*). It was also found in our recent work that a catalyst of MoO_3–P_2O_5, whose atomic ratio P/Mo is in the range of 0.1 ∼ 0.3, is the most effective for the selective oxidation of both butadiene and crotonaldehyde to furan and that, in addition, this system has a fairly stable activity even at 500°C (*9, 10*).

Regarding the binary catalyst system of MoO_3–Bi_2O_3 and the ternary system of MoO_3–Bi_2O_3–P_2O_5, they are well known to be very effective for such allylic oxidations of olefins as that of propylene to acrolein and that of *n*-butene to butadiene. A good deal of work has, therefore, been devoted to the investigation either of the above-cited reactions or of the physicochemical properties of the catalyst system. However, no literature gives definitive information with regard to the effect of Bi_2O_3 addition to MoO_3–P_2O_5 on the catalytic behavior; besides, almost all the work devoted to the oxidation over molybdenum-based catalysts has been limited to investigations under a low oxygen partial pressure, i.e., an equimolar amount or less of oxygen with respect to the olefin.

In the present work, by comparing the data obtained from the oxidation of butene, butadiene, furan, and maleic anhydride over a series of MoO_3–Bi_2O_3–P_2O_5 catalysts varying in their Bi/Mo proportion in the presence of a large excess of oxygen, we attempted to elucidate how the addition of Bi_2O_3 to the MoO_3–P_2O_5 (P/Mo = 0.2 atomic ratio) catalyst affects each reaction step in the consecutive oxidation reactions from butene to maleic anhydride; we attempted also to obtain more detailed information about the variation in catalytic behavior due to the amount of the Bi_2O_3 content in the catalyst.

EXPERIMENTAL

The vapor-phase air oxidation of *cis*-2-butene, 1,3-butadiene, furan, and maleic anhydride was carried out over various molybdenum–bismuth–phosphorus oxide catalysts with different Bi/Mo ratios (P/Mo = 0.2 atomic ratio) in an ordinary continuous-flow-type reaction system at atmospheric pressure. The reactor was a steel tube, 50 cm in length and 1.8 cm in internal diameter, whose surface was coated with aluminium; it was immersed in a molten lead bath whose temperature was controlled by a proportional temperature controller.

The volume concentration of the reactant was about 0.66 mole % in air; the flow rate (at 25°C) was kept at 1.5 liter/min, the amount of the catalyst used was 40 ml; the contact time, which was shown by the volume of the catalyst (ml) per total flow rate (ml/sec), was 1.6 sec. The exit gas leaving the reactor passed first through a series of three hot, and then four cold, packed water bubblers in order to recover the solid and volatile acids and the carbonyl compounds. At the end of 2 hr, the contents of the bubblers were collected and titrated with 0.1 *N* NaOH, using a pH meter. The yields of maleic and other acids were calculated from the titration curves. The feed gas, the exit gas, and the aqueous solution collected by the water scrubbers were analyzed by means of gas chromatography.

The catalysts employed in these experiments were prepared by the following method. The required quantities of ammonium molybdate, bismuth nitrate, and orthophosphoric acid were dissolved in hot water, after which pumice (10–20 mesh) was added; the solution was then evaporated with constant stirring and finally dried in an oven at 130°C. The amount of pumice was 500 ml/g atom of molybdenum and bismuth. The catalysts were calcined under flowing air at 600°C for 10 hr. The P/Mo atomic ratio of the catalysts was kept at 0.2. The surface area of these catalysts was of the order of 3 m^2/g, as determined by the BET method using nitrogen at −195°C.

RESULTS

A. Oxidation of Cis-2-butene

The oxidation of *cis*-2-butene was carried out using a large excess of air over butene at a constant contact time of 1.6 sec over a series of MoO_3–Bi_2O_3–P_2O_5 catalysts, with compositions of Bi/Mo (atomic ratio) = 0, 0.05, 0.10, 0.15, 0.20, 0.3, 0.4, 1.0, 2, 4, ∞. The dependency of the overall butene conversion (the conversion to its isomers is not included) on the reaction temperature is shown in Fig. 1. The results indicate that, under the reaction conditions used here, the activity of butene oxidation is strongly affected by the addition of even a small quantity of bismuth to the MoO_3–P_2O_5 catalyst. It increases with an increase in the bismuth content and goes through a maximum when the Bi/Mo atomic ratio is about 0.10. For example, the MoO_3–Bi_2P_3–P_2O_5 (1:0.1:0.2 atomic ratio) catalyst has about 3.5 times as much oxidation activity at 450°C as the MoO_3–P_2O_5 (1:0.2) catalyst, which is itself more active than the MoO_3-alone catalyst (*10*). However, a further increase in the Bi_2O_3 addition to the MoO_3–P_2O_5 system gradually decreases the activity; for instance, an equiatomic Bi/Mo catalyst, MoO_3–Bi_2O_3–P_2O_5 (1:1:0.2), shows nearly the same activity as MoO_3–P_2O_5 (1:0.2) and Bi_2O_3 alone, and Bi_2O_3-rich catalysts are fairly inactive in butene oxidation.

The oxidation of butene is always accompanied by its isomerization. In the case of a continuous-flow experiment like this,

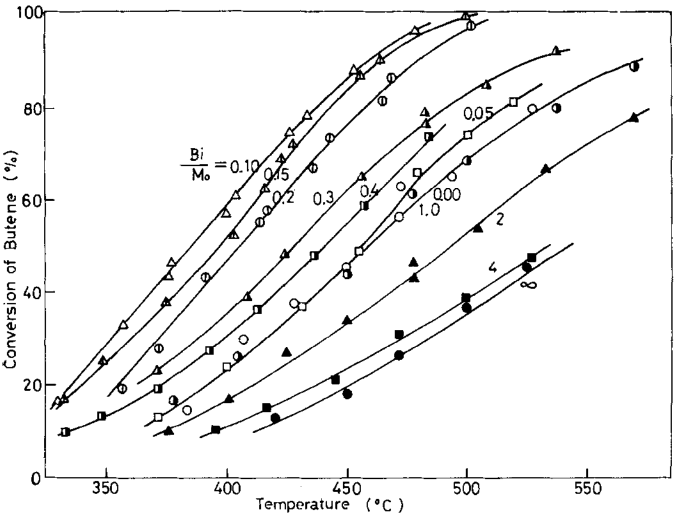

FIG. 1. Dependence of the overall butene conversion on the reaction temperature at various Bi/Mo compositions: ○, Bi/Mo (atomic ratio) = 0; □, 0.05; △, 0.10; ◭, 0.15; ,⊕ 0.2; ▲, 0.3; ◨, 0.4; ◑, 1.0; ▲, 2.0; ■, 4; ●, ∞.

it was observed that, in the absence of oxygen in the feed gas, neither the isomerization of butene nor oxidation occurred (*3, 5*). It can, therefore, be considered that the presence of oxygen is necessary to the isomerization. The sum of the conversion of *cis*-2-butene to such isomers as *trans*-2-butene and 1-butene is plotted as a function of the reaction temperature in Fig. 2. Because the isomerization proceeds to a considerable extent even at a much lower temperature than the oxidation, at lower temperatures only the isomerization is observed. The amount of the isomers increased upon an increase in the temperature; after passing through a maximum, it decreases as a result of the further oxidation of the isomers at higher temperatures. The values of the maximum in the isomer formation increase as the atomic ratio of Bi/Mo increases up to 0.1. However, a further increase in the Bi_2O_3 content decreases it; the Bi_2O_3-rich catalysts also showed very low activity for isomerization.

The formation of butadiene, which could be considered as a primary intermediate in the step-by-step oxidation of butene to maleic anhydride, has been examined. The selectivity of butene to butadiene is shown as a function of the overall butene conversion (excepting isomerization) in Fig. 3. In each case, with increasing the butene conversion the selectivity decreases. As is expected, the maxima in the amount of butadiene formation occur at butene conversions between 50 and 70%, and the value

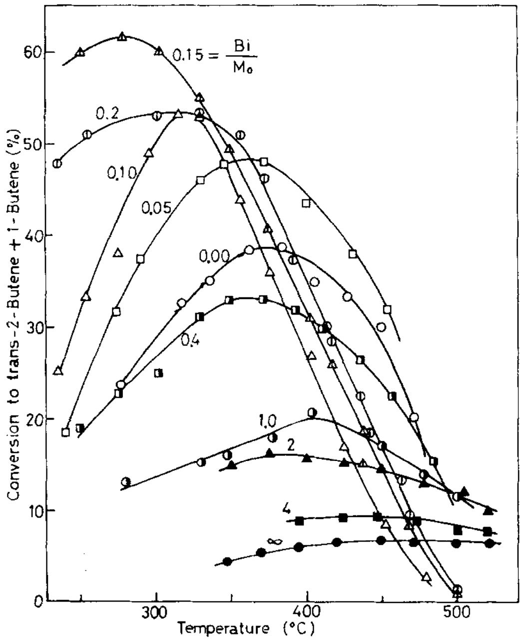

FIG. 2. Sum of the conversion to isomers (*trans*-2-C_4H_8 + 1-C_4H_8) as a function of the reaction temperature: notation as in Fig. 1.

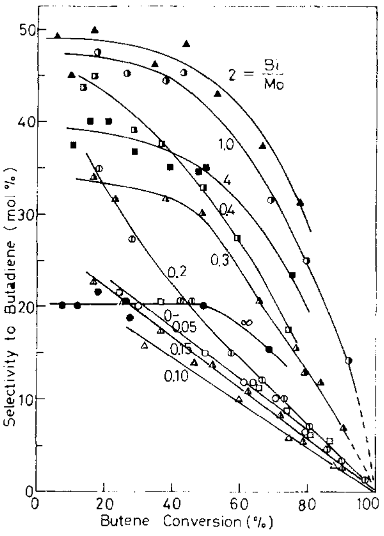

FIG. 3. Selectivity to butadiene as a function of the overall butene conversion: notation as in Fig. 1. The variation in conversion has been effected by changing the temperature (at constant space velocity).

of the butene conversion corresponding to the maximum in butadiene formation tends to be displaced only from 50 to 70%, towards a higher butene conversion, by increasing the content of Bi_2O_3 in the catalyst system. From this fact it can be estimated that regardless of the large variation in the oxidation rate, the variation in the Bi_2O_3 content in the catalyst has comparatively little effect on the rate of butadiene relative to butene.

The selectivity to maleic anhydride over these catalysts is shown as a function of the overall butene conversion in Fig. 4. In each case, with increasing the overall butene conversion the selectivity first increases, goes through a maximum, and decreases to zero. The MoO_3–P_2O_5 catalyst, without Bi_2O_3, gives a relatively low yield of maleic anhydride (about 10 mole % based on the butene fed in); the yield increases greatly with the addition of the Bi_2O_3 to the catalyst. It is optimal at Bi/Mo (atomic ratio) = 0.1 and reaches about 30 mole % at butene conversion of about 85% (selectivity = 34%, based on the butene consumed). It seems that these data are quite as good as the results obtained by the use of molybdenum-based catalysts. The further addition of Bi_2O_3 leads to a remarkable decrease in the yield, and only a little maleic anhydride is obtained over an equiatomic Bi/Mo ratio. The main product in the oxidation over the Bi_2O_3-rich catalysts was CO_2. It was also noted that, over every catalyst, the formation of maleic anhydride decreases at a higher butene conversion. This may be, in part, caused by the further oxidation of maleic anhydride.

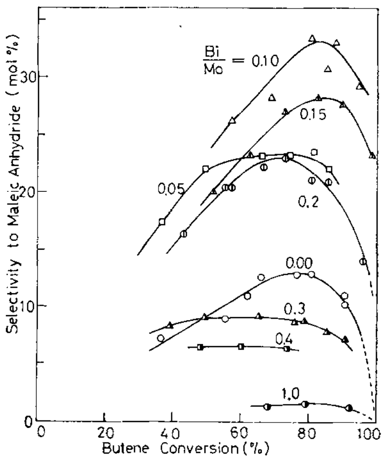

FIG. 4. Selectivity to maleic anhydride as a function of the overall butene conversion: notation as in Fig. 1. The variation in conversion has been effected by changing the temperature (at constant space velocity).

B. Oxidation of Butadiene

Butadiene was oxidized in a manner similar to that used for *cis*-2-butene. The dependency of the butadiene conversion on the reaction temperature is represented in Fig. 5. The activity for butadiene oxidation also increases upon the addition of a small quantity of Bi_2O_3 to the MoO_3–P_2O_5 catalyst; it passes through a maximum at Bi/Mo = 0.1.

The selectivity of butadiene to maleic anhydride at various compositions of the MoO_3–Bi_2O_3–P_2O_5 catalysts is shown as a function of the butadiene conversion in Fig. 6. In each case, the selectivities first tend to increase to a significant extent, with an increase in the butadiene conversion. Similarly to the case of butene oxidation, the formation of maleic anhydride increases even with the addition of a small amount

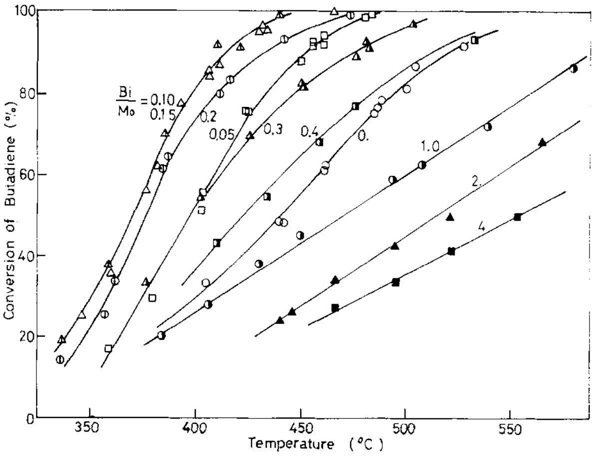

FIG. 5. Dependence of butadiene conversion on the reaction temperature at various Bi/Mo compositions: contact time, 1.6 sec; 0.66% butadiene in air; notation as in Fig. 1.

of Bi_2O_3 to the MoO_3–P_2O_5 catalyst. Optimal results of about 60% (based on the butadiene fed in), are obtained at Bi/Mo = 0.1; with a further addition of Bi_2O_3, the formation of maleic anhydride began to decrease at lower butadiene conversions, so the amount of the maximum formation sharply decreases.

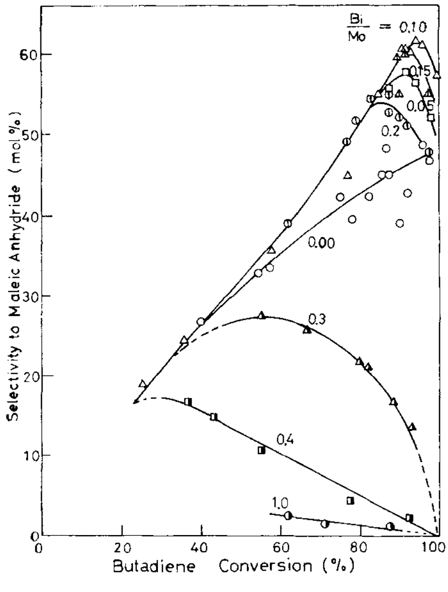

FIG. 6. Selectivity to maleic anhydride as a function of the butadiene conversion: notation as in Fig. 1. The variation in conversion has been effected by changing the temperature (at constant space velocity).

C. *Oxidation of Furan*

Furan is considered as the last intermediate in the consecutive oxidation of butene and butadiene to maleic anhydride which can really be detected (*4*, *7*). The oxidation of furan was tested at various compositions of MoO_3–Bi_2O_3–P_2O_5 in order to clarify the effect of the Bi_2O_3 addition on the $C_4H_4O \rightarrow MA$ step. The dependency of the furan conversion at a constant contact time of 1.6 sec on the reaction temperature is shown in Fig. 7. The results reveal that with the incorporation of Bi_2O_3 to MoO_3–P_2O_5, the oxidation activity for furan varies in a manner similar to those for bu-

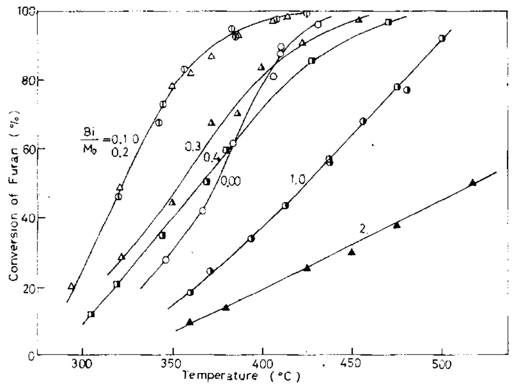

FIG. 7. Dependence of furan conversion on the reaction temperature at various Bi/Mo compositions: notation as in Fig. 1.

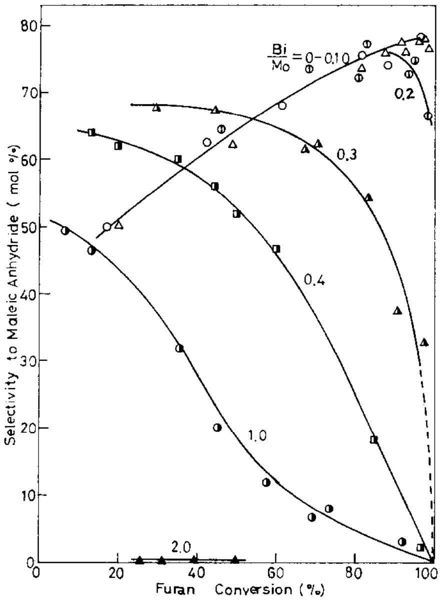

FIG. 8. Selectivity to maleic anhydride as a function of the furan conversion: notation as in Fig. 1. The variation in conversion has been effected by changing the temperature (at constant space velocity).

tene and butadiene, although the former is much higher than the latter.

Figure 8 represents the selectivity of furan to maleic anhydride over the MoO_3–Bi_2O_3–P_2O_5 catalysts. Contrary to the cases of butene and butadiene, the selectivity is relatively high even at a low conversion of the starting material, viz. furan. When the atomic ratio of Bi/Mo is less than 0.1, there is no appreciable change in the maleic anhydride formation and the selectivity increases with furan conversion up to about 80 mole % (the formation based on the furan fed in is about 76%). With the further addition of Bi_2O_3, the selectivity to maleic anhydride begins to fall at lower furan conversions.

D. *Oxidation of Maleic Anhydride*

From the results presented in the preceding sections, it can be suggested that the MoO_3–Bi_2O_3–P_2O_5 catalyst which contains a large amount of Bi_2O_3 has quite a high activity for maleic anhydride degradation with respect to the activity for its formation. We thus attempted to examine the effect on the rate of destructive oxidation for maleic anhydride resulting from the addition of Bi_2O_3 to the MoO_3–P_2O_5 system. The dependency of maleic anhydride conversion on the reaction temperature at a contact time of 1.6 sec is shown in Fig. 9. The results indicate that the MoO_3–P_2O_5 catalyst, without Bi_2O_3 addition, shows an extremely low activity for maleic anhydride oxidation, much like such vanadium-type catalysts as V_2O_5 alone, V_2O_5–P_2O_5, and V_2O_5–MoO_3. However, the activity sharply increased as the Bi_2O_3 contained in the catalyst increased, and a Bi_2O_3-rich or Bi_2O_3-alone catalyst, which has very little

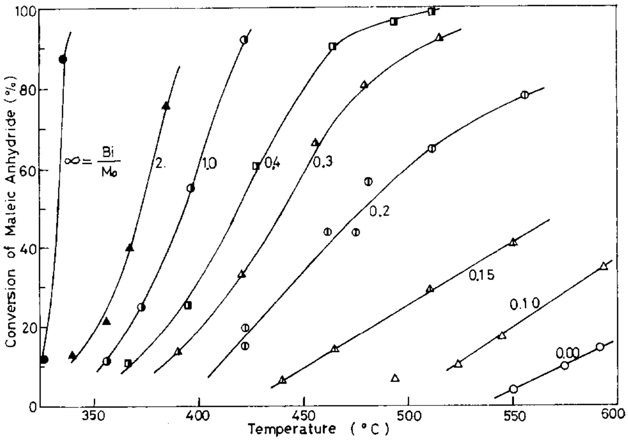

FIG. 9. Dependence of maleic anhydride conversion on the reaction temperature at various Bi/Mo compositions: notation as in Fig. 1.

activity for the oxidation of butene, butadiene, or furan, showed an extremely high activity for maleic anhydride oxidation. Therefore, it is found that, over the catalysts containing a large amount of Bi_2O_3, the rate of maleic anhydride decomposition is much higher than that of its formation.

DISCUSSION

A. *Effect of Bi_2O_3 Addition on the Oxidation Activity*

From the data in Figs. 1, 5, 7, and 9, the relationship between the catalyst composition and the oxidation activity for butene, butadiene, furan, and maleic anhydride is plotted in Fig. 10. The range of activity variation is so wide that it is hard to express it by a reaction rate at a constant temperature. The value of $1000/T_{50}$ is adopted as a measure reflecting the oxidation activity, where T_{50} means the reaction temperature (°K) corresponding to the reactant conversion of 50%. It is found that the catalytic activity for butene, butadiene, and furan varies in the same fashion; the maximum activity for these reactants is obtained at about Bi/Mo (atomic ratio) = 0.1 under the conditions used here. Regarding the oxidation activity of the MoO_3–Bi_2O_3 catalyst, earlier work (*2*, *11*) has indicated that the maximum activity was obtained at about Bi/Mo = 1, although all these data were obtained from oxidations under a poor oxygen atmosphere, a low O_2/hydrocarbon molar ratio. This difference in catalytic behavior may be attributed to a change in the nature of the catalyst surface, for instance, the oxidation state of the catalyst, arising from the variation in the reaction medium.

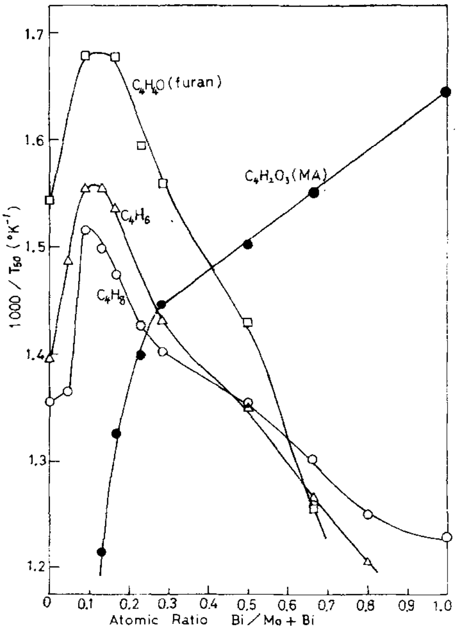

FIG. 10. Oxidation activity ($1000/T_{50}$) versus Bi/(Mo + Bi) ratio: T_{50} is the temperature in °K at which the conversion of the reactants is 50%.

When the Bi_2O_3 content is not so high, i.e., when the atomic ratio of Bi/Mo is in the region below 1, the catalytic activity for butadiene oxidation is a little higher than that for butene, while that for furan is fairly high in comparison with the other two. The order of reactivity is shown as follows; $C_4H_8 < C_4H_6 < C_4H_4O$. This sequence is in agreement over the V_2O_5, V_2O_5–P_2O_5, and V_2O_5–MoO_3 catalysts.

With a further increase in the Bi_2O_3 content, the activity for butadiene decreases more sharply than that for butene. When the Bi/Mo atomic ratio is 1, the two activities happen to be the same, while when the Bi content is more than 50 at.%, the activity for butadiene becomes lower than that for butene. This fact explains why the value of butene conversion corresponding to the maximum butadiene formation is displaced from 50 to 70% towards higher conversions.

On the other hand, a completely different type of curve is obtained in the case of maleic anhydride oxidation; the catalytic activity here increases steadily with an increase in the Bi_2O_3 content.

From the results obtained, it may be supposed that the variation in catalytic activity for these reactants can be attributed to the change in the strength of interaction, i.e., the affinity between the reactant and the catalyst surface. MoO_3 and MoO_3–P_2O_5 are considered to be acidic oxides, like V_2O_5, V_2O_5–MoO_3, and V_2O_5–P_2O_5, while Bi_2O_3 is a basic oxide. On the other hand, the olefins and furan are considered to be basic compounds because of their double bonds.

To explain the results obtained, we assume that the olefins and furan (electron donors) interact easily with such acidic catalysts (electron acceptors) as MoO_3–P_2O_5, MoO_3, V_2O_5–P_2O_5, V_2O_5, V_2O_5–MoO_3, but with difficulty with the basic catalyst, Bi_2O_3. Unlike the olefins and furan, maleic anhydride interacts easily with Bi_2O_3, but with difficulty with acidic oxides. The change in the catalytic activity for each reactant owing to the Bi_2O_3 content can be interpreted in terms of the acid–base nature of the reactant and the catalyst; with an increase in the Bi_2O_3 content, the basicity of the catalyst increases; therefore, the catalyst can interact less easily with the olefins and furan, and more easily with acid (i.e., the activity for the olefins and furan decreases, and that for acid increases).

By taking into account the fact that butadiene is more basic than butene, the difference in their reactivity can also be explained. However, even with this acid–base conception, we cannot yet explain why the activity for olefins and furan reaches a maximum at a Bi/Mo ratio of 0.1.

B. Isomerization of Olefin

The values of the maximum formation of isomers shown in Fig. 2 are employed as a measure reflecting the isomerization activity of the catalysts, and are plotted as a function of the Bi_2O_3 content on the left side of Fig. 11. With the variation in the Bi_2O_3 content, the isomerization activity changes in a manner similar to the oxidation activity for butene, butadiene, or furan, and it passes through a maximum at Bi/Mo = 0.1. An analogous relation of the oxidation–isomerization activity was obtained in the oxidation over alkaline-doped V_2O_5–P_2O_5 catalyst (*12*). The nature of the acidity–basicity of the catalyst may play an equal part in the activities. This may be explained by the mechanism firmly established by Adams and Voge; the first step in the oxidation is the abstraction of a hydrogen atom from the olefin and this stage is common to both the oxidation and isomerization, and it is the rate-determining step of the reaction. This slow stage of allyl intermediate formation is followed by the next two concurrent steps; isomerization and further oxidation. To explain the fact that at a lower temperature the isomerization is predominant with respect to the oxidation, we consider that the activation energy for the isomerization is lower than that for oxidation, and that at a lower temperature the former rate is therefore much higher in comparison with the latter.

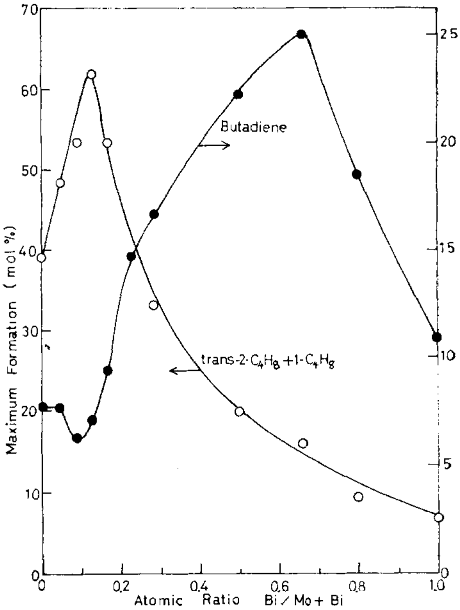

FIG. 11. Maxima formation of the sum of the isomers and butadiene from butene versus Bi/(Mo + Bi) ratio.

C. Effect on the Formation of Butadiene

The shape of the curves in Fig. 3 reveals that butadiene is one of the accumulated primary intermediates in the consecutive oxidation of butene. From the results shown in Fig. 3, the value of the maximum butadiene formation is plotted as a function of the catalyst composition on the right side in Fig. 11. The formation of butadiene increases with an increase in the Bi_2O_3 content and passes through a maximum at Bi/Mo = 1 ~ 2. These results agree with the data in earlier work. It is generally considered that the formation of such an intermediate as butadiene depends on its ease of desorption or further oxidation. This may be governed both by the strength of the interaction between an intermediate and the catalyst and by the relative reactivity of the intermediate to the reactant. When the Bi/Mo ratio is below 2, with an increase in the Bi_2O_3 content both the relative activity of butadiene to butene and the adsorption strength decrease. These facts are favorable to butadiene formation. However, upon a further increase in the Bi_2O_3 addition, the butadiene formation decreases. This is probably to be attributed to the modification of the catalyst species, which leads to a decrease in selectivity for the $C_4H_8 \rightarrow C_4H_6$ step.

D. Effect on the Maleic Anhydride Formation

The fact that the selectivity to maleic anhydride increases with increasing the overall conversion of the starting material (Figs. 4, 6, and 8) may be attributed to the accumulation of butadiene, furan, some polymer products (*4*, *6*), etc. which are formed as precursors of maleic anhydride during the reaction. On the other hand, it is considered that the decrease in the selectivity to maleic anhydride at a higher conversion of the starting material occurs as a result of the further oxidation of produced maleic anhydride. The character of the curves in Figs. 4, 6, and 8 suggests that, with an increase in the Bi_2O_3 content in the catalyst, the activity for the destructive oxidation of maleic anhydride increases and an appreciable secondary oxidation of maleic anhydride occurs, even at lower reactant conversions.

From the data in Figs. 4, 6, and 8, the values of the maximum formation of maleic anhydride from butene, butadiene, and furan are plotted as a function of the catalyst composition in Fig. 12. Over the whole range of Bi/Mo ratios, the yield of maleic anhydride is in the order: $C_4H_8 < C_4H_6 < C_4H_4O$; this is reasonable when we take into acount that the reaction proceeds as follows: $C_4H_8 \rightarrow C_4H_6 \rightarrow C_4H_4O \rightarrow MA$.

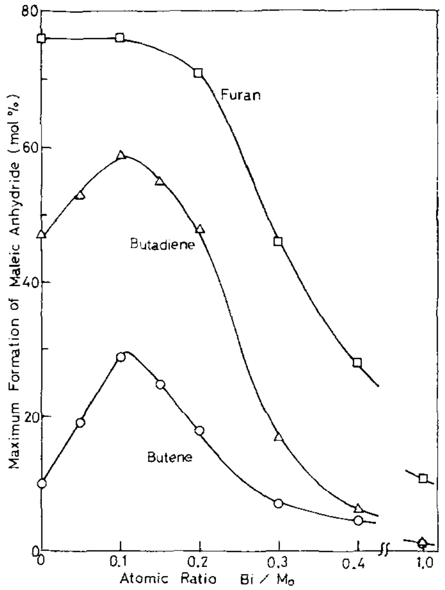

FIG. 12. Maximum formation of maleic anhydride versus Bi/Mo ratio.

The curves of butene and butadiene follow the same trend, and their shapes are quite similar to those of the oxidation activities for butene, butadiene, and furan shown in Fig. 10. The maxima are still present at the Bi/Mo atomic ratio of about 0.1. On the other hand, in the case of furan oxidation, there is no appreciable change in the maximum maleic anhydride formation when the atomic ratio of Bi/Mo is below 0.1. These facts indicate that the presence of a small amount of Bi_2O_3 serves to increase the selectivity in the cyclization step ($C_4H_6 \rightarrow C_4H_4O$) as well as in the $C_4H_8 \rightarrow C_4H_6$ step. The decrease in maleic anhydride formation which occurs upon the further addition of Bi_2O_3 is attributable to the fact that the activity for the secondary oxidation of maleic anhydride grows to a significant extent, thus no longer being negligible.

It can be concluded, finally, that the best results, in regard to both the oxidation activity and the yield of maleic anhydride, are obtained at the Bi/Mo ratio of 0.1 in the oxidation of butene and butadiene. The yields of maleic anhydride from butene, butadiene, and furan reach 30, 60, and 76 mole %, respectively, based on the reactants fed in.

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