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# The Catalytic Oxidation of Propylene

## II. Iron-Based Bismuth Molybdate Catalysts for the Partial Oxidation of Propylene

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Catalysts containing bismuth, molybdenum, and iron were prepared by a slurry method. They were formed by reacting the α-phase of bismuth molybdate, i.e., $Bi_2O_3$–$3MoO_3$, with $Fe(OH)_3$. The catalysts so formed exhibited activity and selectivity comparable to bismuth molybdate for the oxidation of propylene to acrolein. The activity and selectivity of the Bi–Mo–Fe catalysts tested at 400°C were unchanged after running them under highly reducing conditions or by pretreating them at 800°C for 12–24 hr. It is suggested that the Bi–Mo–Fe catalysts attain their catalytic behavior from the formation of a distinct chemical compound or structure, formed in the reaction between the α-phase of bismuth molybdate and $Fe(OH)_3$.

### INTRODUCTION

Various bismuth molybdate catalysts have been reported for the partial oxidation and ammoxidation of propylene. Extensive work in this area is no doubt due to the successful commercialization of the acrylonitrile process based on a bismuth phosomolybdate catalyst by SOHIO (*1*).

More recently, other catalyst systems have begun to attract considerable attention. The SOHIO workers developed a uranium–antimony catalyst which also achieved commercial success (*2*, *3*). Japanese workers (*4*, *5*) have reported the results of a study on a catalyst composed of Bi–Mo–Sb. They claim that this catalyst shows better selectivity and activity for the ammoxidation of propylene than does the bismuth phosomolybdate catalyst. Multicomponent catalysts containing Bi, Mo, and Fe as the principal ternary combination also appear to be active catalysts for the oxidation and ammoxidation of propylene. Such catalyst systems containing Bi–Mo–Fe have been described in the patent literature (*6*, *7*) but little information regarding this system is available in the journal literature (*8*).

We decided to study this promising combination and would now like to report the preliminary results of our investigation on the Bi–Mo–Fe catalyst. We have varied the iron content in the preparation and have tested the catalytic activity and selectivity of the resultant catalysts. We also have compared the activity and selectivity of the Bi–Mo–Fe catalyst with a bismuth molybdate catalyst and pure iron oxide.

### EXPERIMENTAL

#### *Catalyst Preparation*

All of the chemicals used in the preparation of the catalysts were of analytic grade.

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Because it has been our experience, as well as that of others (*9–11*), that simple precipitation methods often produce ill defined catalysts, we decided to prepare the Bi–Mo–Fe catalyst by the slurry method described by Batist (*12*). This method is simply the heating to dryness of an aqueous paste of the reactants. During the heating process, reactions occur which produce the final form of the catalyst.

More specifically, we decided to attempt to react iron hydroxide, $Fe(OH)_3$, with the pure $\alpha$-phase of bismuth molybdate, i.e., with $Bi_2O_3$–$3MoO_3$. (We plan to report the results of a detailed investigation of the preparation and the identification of the pure $\alpha$- and $\gamma$-forms of bismuth molybdate in a future communication.) The $Fe(OH)_3$ was prepared from $Fe(NO_3)_3 \cdot 9H_2O$ by precipitation with dilute $NH_4OH$. The $Fe(OH)_3$ precipitate was washed thoroughly with distilled water to free it from nitrate ion. Various ratios of Fe as $Fe(OH)_3$ were then added to the $\alpha$-phase of bismuth molybdate to form the slurries, which were heated to dryness on a hot plate over a period of 10–15 hr. After calcining at 600°C for 6 hr, the catalysts were ground and sieved to 8–14 mesh. The four catalysts prepared by this method and studied in the present investigation had the following Bi/Mo/Fe atomic ratios: 27.6/41.4/31; 24/36/40; 21/31.6/47.4; and 14.3/21.4/64.3.

The iron oxide which was used as a catalyst was prepared by drying the $Fe(OH)_3$ precipitate and then calcining at 460°C for 6 hr.

The bismuth molybdate catalyst used in the experiments was prepared by dissolving $Bi(NO_3)_3 \cdot 5H_2O$ (29.16 g) in 200 ml of distilled water containing 10 ml of conc $HNO_3$ at 25°C. A second solution was made by dissolving $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (10.59g) in 200 ml of distilled water at 25°C. The second solution was slowly added to the first with constant stirring. The pH of the solution was then increased to pH 6 by adding solid $(NH_4)_2CO_3$. The solution was filtered and the precipitate washed with 600 ml of distilled water. After drying the precipitate at 120°C for 6 hr, it was calcined in air at 450°C for 4 hr.

### *Apparatus*

A single-pass, integral-flow reactor operating at atmospheric pressure was used in all of the experiments. Details of its construction have been published previously (*13*). Propylene, oxygen, and helium were passed through micron filters and molecular sieve traps. The flow rates of the three gases were controlled with microneedle valves and were used in the ratio 60/45/30 cc (STP)/min. The gas mixture was subsequently homogenized by passage through a spherical mixing volume prior to the reactor.

Because the catalyst samples were found to be very active, only 0.25 cc of the catalyst was packed in the tube. To minimize the possibility of homogeneous reactions (*14*), both the precatalytic and the postcatalytic volumes were packed with Pyrex wool. Reaction temperature was maintained at 400°C by a proportional temperature controller. The products obtained after steady state conditions had been reached were analyzed by a gas chromatograph containing both a Poropak Q-S column and a molecular sieve 5A column.

## RESULTS AND DISCUSSION

The catalysts obtained by the slurry method described earlier were hard, homogeneous solids. It should be noted, however, that with smaller iron ratios than those reported herein, the catalytic mass appeared to be a mixture. In the apparent mixtures, white to light-yellow particles were observed along with a brown solid. Presumably, these light-colored particles are the unreacted $\alpha$-phase of bismuth molybdate or possibly $MoO_3$ and/or $Bi_2O_3$. It should also be pointed out that thermal treatment at temperatures up to 900°C of a mixture of $Bi_2O_3$–$3MoO_3$ and $Fe_2O_3$ did not produce a homogeneous mixture. Also, when the $\gamma$-form of bismuth molybdate, $Bi_2O_3$–

$MoO_3$, was reacted with $Fe(OH)_3$ a mixture was formed instead of a homogeneous solid. Consequently, we have concluded that the active form of the catalyst represents a well defined compound with a specific structure formed in the reaction of $Bi_2O_3$–$3MoO_3$ with $Fe(OH)_3$. We presently are investigating this possibility by X-ray methods.

A comparison of the activity and selectivity for the various Bi–Mo–Fe catalysts, bismuth molybdate, and iron oxide is presented in Table 1. At the same temperature and flow composition, the Bi–Mo–Fe catalysts exhibit a higher conversion than the bismuth molybdate catalyst. However, the product distribution for the Bi–Mo–Fe resembles quite closely that obtained with the bismuth molybdate catalyst. Hence, we interpret this to mean that mechanistically these catalysts maintain their ability to form an allyl species, as has been shown to be the important feature of the bismuth molybdate system. This point is further clarified in comparing their product distribution with iron oxide. Iron oxide is not commonly referred to as a catalyst for acrolein formation via an allyl species, and by examining the product distribution it is clear that it is effective mainly for the complete combustion reaction.

To a first approximation then, we conclude that the Bi–Mo–Fe catalysts mechanistically resemble bismuth molybdate catalysts. It is interesting to note that when we tested a physical mixture of iron oxide and bismuth molybdate, the product distribution resembled that of the iron oxide. Consequently, we feel that had not the iron actually reacted with the bismuth molybdate to form a new phase, but instead had it remained as the oxide, we would have observed a product distribution that resembled quite clearly that of the iron oxide.

As the Fe content increases, the total activity increases until the Bi/Mo/Fe ratio reaches 21/31.6/47.4, after which the total activity and selectivity decline. Concomitant with the increase in Fe content is an increase in the selectivity for Co and $CO_2$. This may be due to the presence of pure iron oxide in the mixture, but visual examination indicated that the mass was homogeneous. As indicated earlier, experiments are now underway to explore this possibility further.

We would like to suggest that the increased amount of $CO_2$ formed with the Bi–Mo–Fe catalyst reflects a slight change in the mechanism of the reaction of the surface allyl species as compared with bismuth molybdate. As has been shown for the bismuth molybdate system, a large fraction of the acrolein formed is produced via a process utilizing lattice oxygen

TABLE 1

Comparison of the Product Distribution for a Series of Bi–Mo–Fe Catalysts[a]

| Catalyst composition (Bi/Mo/Fe) | 27.6/41.4/31 | 24/36/40 | 21/31.6/47.4 | 14.3/21.4/64.3 | $Fe_2O_3$ | Bi-Mo |
|---|---|---|---|---|---|---|
| Temperature, °C | 400 | 400 | 400 | 400 | 400 | 400 |
| Products[b] | | | | | | |
| CO | 26 | 52 | 49 | 70 | 67 | 13 |
| $CO_2$ | 31 | 30 | 66 | 88 | 179 | 21 |
| $H_2C{=}CH_2$ | 0 | 1 | 3 | 2 | 1 | 3 |
| Acetaldehyde | 3 | 2 | 3 | 2 | 0 | 17 |
| Acrolein | 88 | 76 | 65 | 59 | 12 | 75 |
| Conversion, % | 14 | 19 | 27 | 21 | 18 | 9 |

[a] All experiments were run with 0.25 cc of catalyst and with a total gas flow of 125 cc (STP)/min. The gas composition was $C_3H_6$:48%, $O_2$:36%, He:16%.

[b] Moles of product formed per 100 mole of $C_3H_6$ reacted.

atoms (*15, 16*). The kinetics indicate a zero-order dependence on oxygen pressure. With the Bi–Mo–Fe catalysts, on the other hand, we have found a first-order kinetic dependence on oxygen pressure (*17*), which we have suggested earlier to indicate a reaction between the surface allyl species and chemisorbed oxygen, rather than lattice oxygen (*14*). The decomposition of the surface species produces acrolein and $CO_2$. Furthermore, in contrast to bismuth molybdate, we have observed that CO is oxidized to $CO_2$ over the Bi–Mo–Fe catalyst, again indicating a mechanistic change.

Finally, in contrast to bismuth molybdate, the Bi–Mo–Fe catalysts maintain their activity and selectivity for acrolein under highly reducing conditions. In fact, we have not been able to reduce significantly their activity by running under highly reducing conditions. And when the original conditions were reestablished the activity and selectivity returned to their prior values. Furthermore, high temperatures do not cause a decline in the catalytic activity of the Bi–Mo–Fe catalysts. We have heat treated these catalysts in air at 800°C for 12–24 hr, and have found no change in their activity or selectivity. These two observations increase our tendency to believe that a definite chemical compound incorporating Bi, Mo, and Fe has been formed and that the stability and the catalytic activity of the Bi–Mo–Fe catalysts are due to this compound. In summary, it appears that the Bi–Mo–Fe catalysts prepared from the $\alpha$-phase of bismuth molybdate and $Fe(OH)_3$ are promising catalysts for the catalytic oxidation and ammoxidation of olefins.

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