

The Oxidation of Propene over Bismuth Oxide, Molybdenum Oxide, and Bismuth Molybdate Catalysts

I. The Preparation and Testing of the Catalysts

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This part describes the preparation and testing, in a flow system, of the supported and unsupported catalysts bismuth molybdate, molybdenum oxide, and bismuth oxide which were used for the ESR, electrical conductivity, and kinetic studies described in parts II, III, and IV.

INTRODUCTION

The industrial importance of mixed oxides of molybdenum and bismuth as heterogeneous catalysts for the selective oxidation of hydrocarbons has led to many studies of the best conditions of operation and to considerable speculation on the mechanisms of the reactions involved (1). The unsupported and silica-supported bismuth molybdates, suitably activated, were shown (2, 3) to be highly selective catalysts at 450–500°C for the oxidation by air of propene to acrolein and of *n*-butenes to butadiene, and they show sustained high activity over wide variations of flow rates and hydrocarbon-air ratios. The oxidations over bismuth molybdates (6), (2), the oxidation of 1-pentene to 1,3-pentadiene (4) and the oxidative ammonolysis of propene to acrylonitrile (5) show similar features. Adams recently reported upon exploratory work on other oxidations over bismuth molybdates (6).

The kinetics of the oxidation of C₃ and C₄ olefins together with studies of the concurrent isomerization of 1-butene to *cis*- and *trans*-2-butene (3), and the results of experiments involving olefins labeled with ¹⁴C or ¹³C (7) or deuterium (8), have led to the generally accepted view

that the first step in the catalytic oxidation is the abstraction of hydrogen from the olefin to yield a chemisorbed allyl (or substituted allyl) species. This is followed by further oxidation by lattice oxygen or, as more commonly thought, by chemisorbed oxygen, the selectivity depending on the relative ease of desorption or further oxidation of the partially-oxidized chemisorbed species.

Previous investigators have also studied the dependence of the activity and selectivity of the oxidations upon the composition and pretreatment of the catalysts. For propene oxidation, MoO₃ alone shows a high activity but poor selectivity, Bi₂O₃ is relatively inactive and nonselective, but the mixed oxide catalysts are both highly active and selective. Studies of the phase diagram of the Bi₂O₃-MoO₃ systems have established the existence of a number of intermediate stable phases, e.g., Bi₂O₃·3MoO₃, Bi₂O₃·MoO₃, and 3Bi₂O₃·MoO₃ (9). However, the mixed oxides are active over so wide a range of Bi/Mo ratios [e.g., 0.4–2.0 (10)] and their activities vary so much with the method of preparation, that it does not seem fruitful to attempt correlations between the activity of the catalysts and their phase diagrams determined under noncatalytic conditions. This point of view is reinforced by detailed X-ray studies (11) of the mixed

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oxide catalysts which show changes of structure with precalcination temperature, and also abrupt structure changes with temperature when the catalyst is studied under operating conditions in propene-air mixtures (12).

The work described in the present series of four papers originated in attempts to identify by infrared spectroscopy the species formed by chemisorption of propene on various active catalysts prepared as described below. Parallel studies were made of a lower oxidation state (Mo^{5+}) of molybdenum in the catalysts under reaction conditions, using electron spin resonance spectroscopy. The ESR work, described in Part II, revealed considerable differences in the behavior of the Mo^{5+} signals from bismuth molybdate and molybdenum oxide catalysts as the reaction conditions were changed. The infrared studies, however, yielded very little information because the catalysts, when exposed to propene or butene or hydrogen, rapidly became opaque to those IR frequencies of interest. The electrical conductivity of the catalysts changed rapidly and reproducibly on exposure of catalyst specimens to reducing or oxidizing conditions, and the investigations described in Part III not only reveal the cause of the onset of IR opacity but also give very useful information about the state of reduction of the catalysts under operating conditions. Finally, low-pressure mass-spectrometric studies of the reactions of propene and other reducing agents with the catalysts, in the absence or presence of gaseous oxygen, show some very interesting changes of selectivity with the state of reduction of the catalyst surfaces. This work, described in Part IV, when combined with the results of the electron spin resonance and electrical conductivity measurements, allow some speculation upon the causes of improved selectivity in the presence of bismuth and under certain reaction conditions.

THE PREPARATION OF THE CATALYSTS

Supported and unsupported catalysts were prepared and tested in a flow system

to ensure that the IR, ESR, and conductivity measurements were made on realistic catalyst specimens. It soon became apparent that for ESR studies it was essential to use ultrapure reagents, and only these preparations are described.

Catalysts SBM-3, SM-2, and SB-2 Supported on "Aerosil" Silica

To prepare SBM-3, supported bismuth molybdate, 45 g of pharmaceutical grade ammonium molybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (Merck Chemicals no. 1182), were ground to a powder and dissolved in 50 ml of ultrapure water, and 20 ml of specially prepared 0.88 ammonia solution were added. This mixture was added to 960 ml of a 10% suspension of "aerosil" silica in ultrapure water. A 91-g portion of bismuth nitrate, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Merck Chemicals no. 1860), was ground to a powder and dissolved in 110 ml of 5 M nitric acid. This solution was added to the silica-ammonium molybdate mixture and the solution was vigorously stirred. Precipitation of the bismuth molybdate was achieved by slowly running 10 M ammonium hydroxide into the mixture until pH 5 was obtained. The paste was heated to dryness and the resultant pale green solid finally was dried at 120°C for 24 hr, followed by activation in a stream of air at 530°C for 16 hr. The resultant activated catalyst was pale yellow in color, contained 56% (w/w) of silica, and had $\text{Bi}:\text{Mo} = 0.74:1.00$. The BET surface area was 70 m^2g^{-1} (of catalyst plus support).

Supported molybdenum oxide, SM-2, and supported bismuth oxide, SB-2, were similarly prepared and dried to constant weight at 120°C in air, and were activated by heating in air at 530°C for 20 hr. Each preparation contained 75% (w/w) of silica; SM-2 was pale lemon and SB-2 pale yellow in color.

Unsupported Catalysts UBM-2, UBM-4, UM-3, and UB-3

Unsupported bismuth molybdate UBM-2 was prepared as described for SBM-3, ex-

cept that silica was excluded. The BET area was $1.5 \text{ m}^2\text{g}^{-1}$ and Bi:Mo = 0.74:1.00.

The UBM-4 was prepared by a dry method described by Cornaz *et al.* (14). A 9-g portion of bismuth nitrate (Merck 1860) was mixed with 4.5 g of ammonium molybdate (Merck 1182) in a platinum crucible, and the pale green mixture was heated gently in a furnace to 300°C . The yellow solid was cooled, ground, and heated for 6 hr at 500°C . Finally, the sample was activated in a stream of oxygen at 530°C for 20 hr. The specific surface area (BET) was $1 \text{ m}^2\text{g}^{-1}$ and Bi:Mo = 0.73:1.00.

UM-3. Ammonium molybdate (Merck 1182) was heated at 100°C to decompose the salt and remove the water of hydration. The pale blue solid was heated at 530°C in air for 20 hr and after this activation was pale lemon in color.

UB-3. Bismuth nitrate (Merck 1860) was heated to decompose the salt and the resulting yellow oxide was heated in air at 530°C for 20 hr.

PREPARATION OF THE GASES

Research grade propene (Cambrian Chemicals Ltd.) was transferred from a cylinder to a trap in liquid nitrogen and was degassed three times. The cut taken from the final degassing contained less than 0.2% impurities (chiefly propane). This purified gas was used for all work except the preliminary catalyst testing, where commercial propene containing 96% C_3H_6 (impurities 3.7% propane and traces of butenes and hydrogen), kindly supplied by Shell Chemicals, was used directly from the cylinder.

Propane, 1-butene, and 1,3 butadiene (Cambrian Chemicals Ltd.) were purified as described for propene. Their purity was better than 99.8%.

Oxygen, nitrogen, hydrogen, and argon (B.O.C.) were used directly from cylinders. All were better than 99.9% pure except oxygen, which contained 0.4% argon and 0.1% nitrogen.

Carbon monoxide and carbon dioxide (B.O.C. grade X) were spectroscopically pure and were used directly.

Acrolein was freshly distilled in a blacked-out vacuum system from the "Analar" liquid into darkened bulbs and traps, frozen, degassed twice, and the middle cut was collected. The product was used immediately, in darkened vacuum lines, to avoid polymerization.

TESTING OF THE CATALYSTS

Samples of the catalysts were tested (13) in a simple flow system for their activity and selectivity in the oxidation of propene to acrolein, before being used in the IR, ESR, and electrical conductivity experiments. The system was blacked-out to prevent photopolymerization of acrolein. The composition of mixtures was determined mass-spectrometrically.

About 0.5 g of catalyst (powdered to 100–200 mesh) was placed between glass wool plugs in an electrically heated tubular vessel. Propene, oxygen, and argon were preheated to the reaction temperature and mixed rapidly before entering the vessel. The flow rates were adjusted to give 1 liter/hr of C_3H_6 plus O_2 and 4 liters/hr of argon, at a total pressure of 1 atm; this gave residence times over the catalyst of about 0.4 sec. Argon was used as diluent instead of nitrogen to allow analysis of CO and to act as an internal reference peak. The exit gases from the reactor were rapidly cooled and sampled by an indirect lead to an A. E. I. type MS10 mass spectrometer. A stainless steel capillary (bore 0.05 cm and length 180 cm) delivered a continuous sample to an interspace evacuated to about 2×10^{-2} torr by a 2-stage rotary pump and gas leaked from this interspace through a ceramic leak into the MS10. The inlet capillary was maintained at 130°C to prevent condensation of products. The analyses were complicated by the production of small amounts of CO and CO_2 from carbon deposited in the rhenium filament of the ion source and in the tungsten filament of the ionization gauges from decomposition of hydrocarbons; these appeared with pure oxygen; in addition, further small amounts were formed by oxidation of the propene at the filaments. Corrections were applied (13)

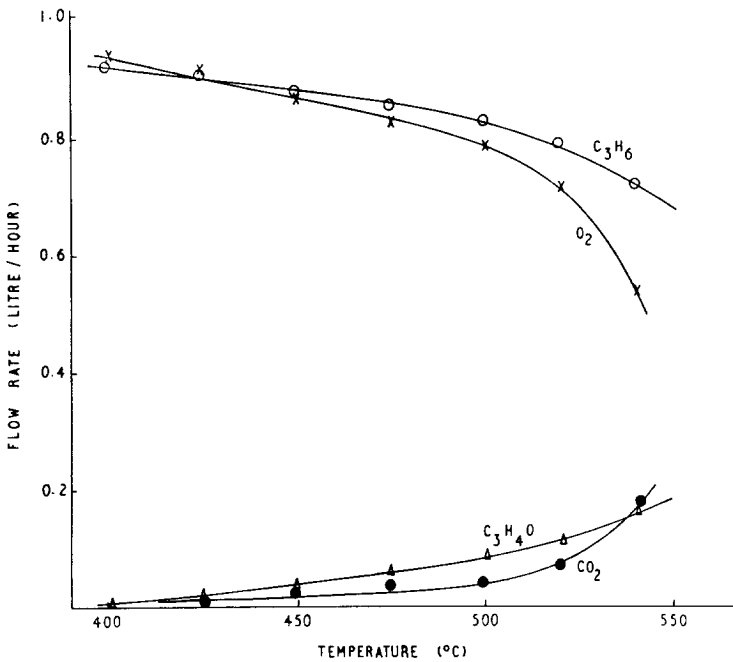


FIG. 1. Composition of exit gas with temperature for SBM-3; residence time 0.4 sec.

using data from "cold" C_3H_6/O_2 mixtures. pene occurred through thermal reactions at the highest temperatures used. The

Blank runs without the catalyst showed that less than 3% conversion of the pro- catalyst temperature, measured by a chromel-alumel thermocouple immersed in

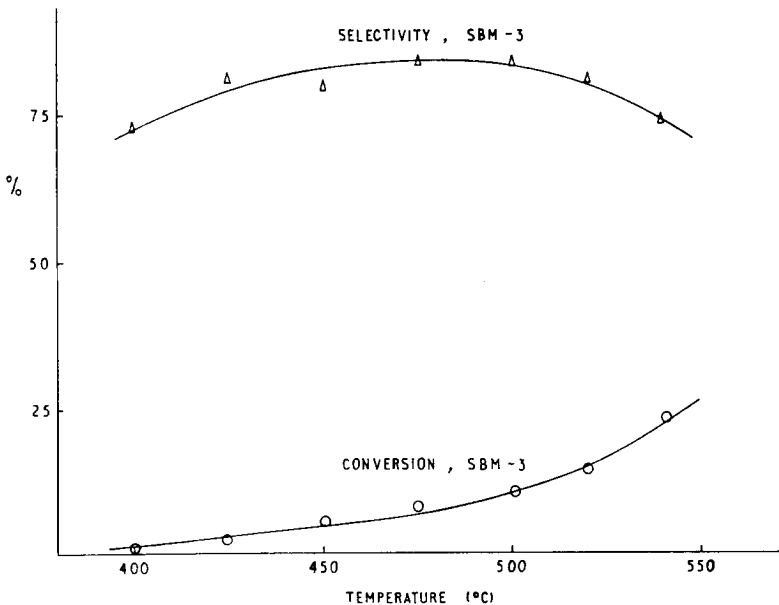


FIG. 2. Variations of percentage conversion and percentage selectivity with temperature for SBM-3; residence time 0.4 sec.

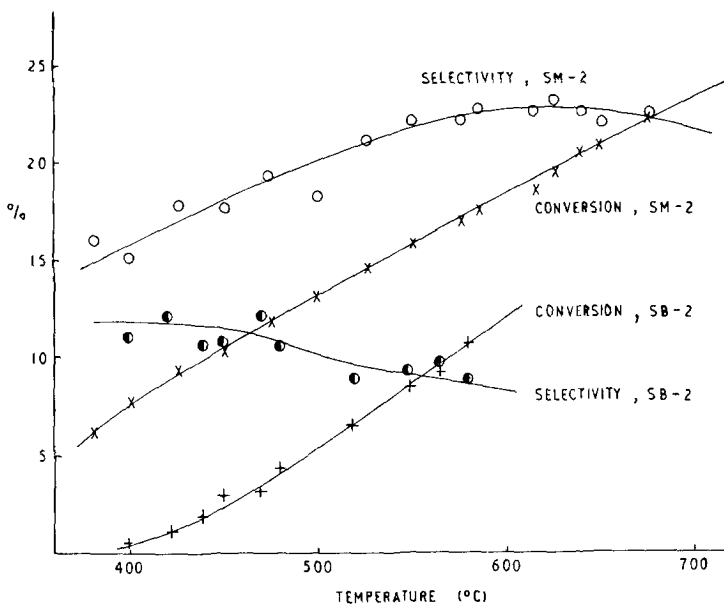


FIG. 3. Variations of percentage conversion and percentage selectivity with temperature for SM-2 and SB-2; residence time 0.4 sec.

the catalyst powder, showed significantly higher temperatures than the furnace at the faster rates of oxidation observed at the higher reaction temperatures.

RESULTS AND DISCUSSION

The results shown in Figs. 1, 2, and 3 summarize the tests on SBM-3, SM-2, and SB-2.

Figure 1 shows the primary data obtained for SBM-3 for the residence times of about 0.4 sec. The conversion to C_3H_4O increased steadily as the temperature increased, but relatively more CO_2 was formed at temperatures above $500^\circ C$; the amounts of CO were low throughout. In contrast, on SM-2 approximately equal amounts of CO and CO_2 were formed at each temperature. Carbon and oxygen balances were constructed assuming that any hydrogen not accounted for as C_3H_6 or C_3H_4O had formed water, and agreed to better than $\pm 5\%$ in all cases examined. This agreement, and the absence of mass-spectrometric peaks corresponding to other partial-oxidation products, suggest that the mass-spectrometric analyses used here

and in Part IV can be treated with confidence.

Figures 2 and 3 show the percentage conversion (represented as $-100\Delta[C_3H_6]/[C_3H_6]$) and the percentage selectivity ($-100\Delta[C_3H_4O]/\Delta[C_3H_6]$, where $\Delta(X) = (X)_{final} - (X)_{initial}$), at various catalyst temperatures. Similar results were found for the unsupported catalysts, though the conversions at each temperature were naturally different because of the different surface areas of the samples.

The bismuth molybdate catalyst, SBM-3, showed high selectivity for acrolein (70–80% at these flow rates, which were not optimal) at all temperatures, and increasing activity with increasing temperature. Virtually identical results were obtained (13) with UBM-4 catalysts. The molybdenum oxide SM-3 showed comparable activity to SBM-3, but much lower selectivity (15–25%), while the bismuth oxide showed still lower selectivity (10%) and much lower activity.

These results clearly show that the catalysts used in the present work are typical of those studied by previous in-

investigators, and in consequence justify attempts to correlate the ESR, electrical conductance, and kinetic data obtained in the present studies with other investigations (1).

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