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Stability of Bismuth Molybdate Catalysts at Elevated Temperatures in Air and under Reaction Conditions

THOMAS P. SNYDER[1] AND CHARLES G. HILL, JR.[2]

Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin 53706

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The stability of bismuth molybdate catalysts during use for the partial oxidation of propylene has been investigated *in situ* using Raman spectroscopy and a novel reactor cell. These studies were supplemented by X-ray diffraction analyses. A phase change of 5% was detectable via Raman spectroscopy at 400°C, and a phase change of 2% could be seen at room temperature. Evidence has previously been reported for the occurrence of alterations in the structure of bismuth molybdate catalysts which were seen only under reaction conditions. In this study it was found that the alpha, beta, and gamma phases of bismuth molybdate were all completely stable under the conditions normally employed for the catalytic partial oxidation reaction. The reasons underlying conflicting opinions concerning the thermodynamic stability of beta bismuth molybdate have been discovered and the conflict resolved. This *in situ* investigation of the stability of bismuth molybdates is the first to have been conducted under conditions normally employed for the catalytic partial oxidation of propylene.

INTRODUCTION

Bismuth molybdates and other mixed metal oxide catalysts are frequently employed to effect the partial oxidation or ammoxidation of light hydrocarbons to produce such important chemical intermediates as acrolein, acrylonitrile, methacrolein, and butadiene. Several general reviews of research on catalytic partial oxidation processes in their various manifestations are available in the literature (*1–13*), including a recent contribution from our group (*14*) which focuses on the mechanism for the partial oxidation of propylene over bismuth molybdate catalysts.

In spite of the "classic" role which bismuth molybdates play in studies of heterogeneous catalytic partial oxidation reactions, many unanswered questions persist as to both the nature of the solid phase present under reaction conditions and the manner in which it participates in these reactions. The present paper summarizes the results of our efforts to address the question of what solid phases are present under the reaction conditions normally employed by industry.

Over the past two decades a large amount of piecemeal information concerning solid phase reactions between specific forms of bismuth molybdates and their parent oxides, MoO_3 and Bi_2O_3, has become available. Said data have often been limited to narrow temperature regions and/or narrow ranges of composition. Erman *et al.* (*15*) were the first to report a complete phase diagram encompassing those phases which have significant catalytic activity for the partial oxidation of propylene. The two most recent phase diagrams are shown in Figs. 1 and 2. Table 1 summarizes the stoichiometric compositions of the various solid phases which are generically labeled as bismuth molybdates. While the diagram of Chen and Smith (*16*) is less detailed than that of Egashira *et al.* (*17*), the two are largely in agreement. The important exception is that

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[1] Current address: Chevron Research Laboratories, 576 Standard Avenue, Richmond, CA 94802-0627.

[2] To whom correspondence should be addressed.

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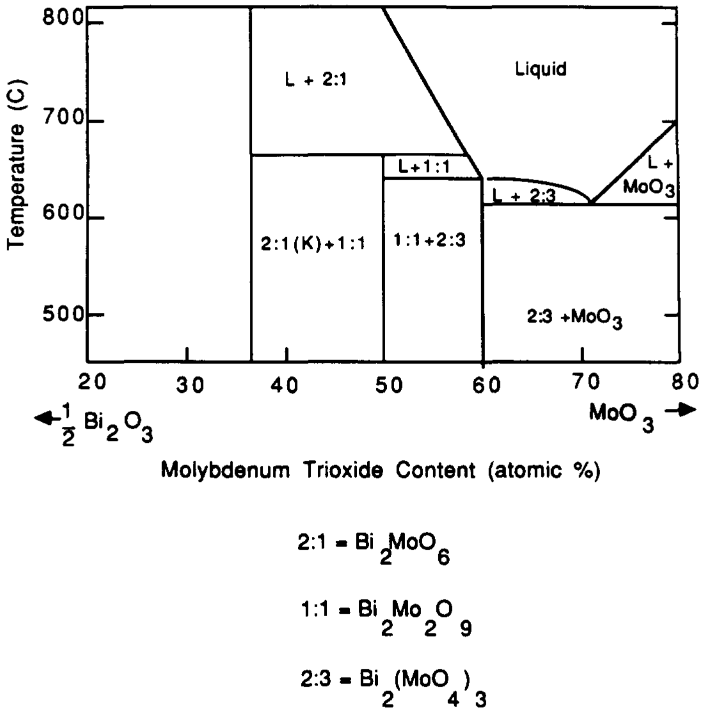

FIG. 1. Phase diagram for the bismuth molybdate system adapted from Chen and Smith (*16*).

while Chen and Smith report that the beta phase is stable below 660°C, Egashira *et al.* report that the beta phase disproportionates into gamma and alpha phases below 540°C. It was on this and other questions concerning the stabilities of the various solid phases of the bismuth molybdates that the present research effort was focused.

Relative Stabilities of Bismuth Molybdates in Air

The solid state reaction between gamma bismuth molybdate and alpha bismuth molybdate to form beta bismuth molybdate and the reactions by which beta bismuth molybdate may decompose to form gamma bismuth molybdate in combination with either MoO_3 or alpha bismuth molybdate have been studied by several authors (*15, 17–25*). The key results of relevant investigations are summarized in Table 2.

Examination of Table 2 reveals conflicting results for the stability of the beta phase bismuth molybdate. Our own experience has shown that there are some important differences between reactions occurring in fresh mixtures of coprecipitated bismuth molybdate phases and reactions occurring in mixtures of phases where the components of the mixture have been separately prepared and calcined above 500°C prior to mixing. Early on we were confused by apparently conflicting results reported in the literature. For example, Egashira *et al.* (*17*) reported that beta bismuth molybdate will decompose on prolonged heating below 530°C. This result is in direct conflict with the result of Monnier and Keulks (*25*) who found that beta bismuth molybdate which had been prepared "by the method of Gryzbowska (*23*)" was stable between 300 and 470°C. What is important to note here is that both authors were unclear in their reports concerning what now appears to be a very important factor in the stability of beta bismuth molybdates, i.e., the thermal history

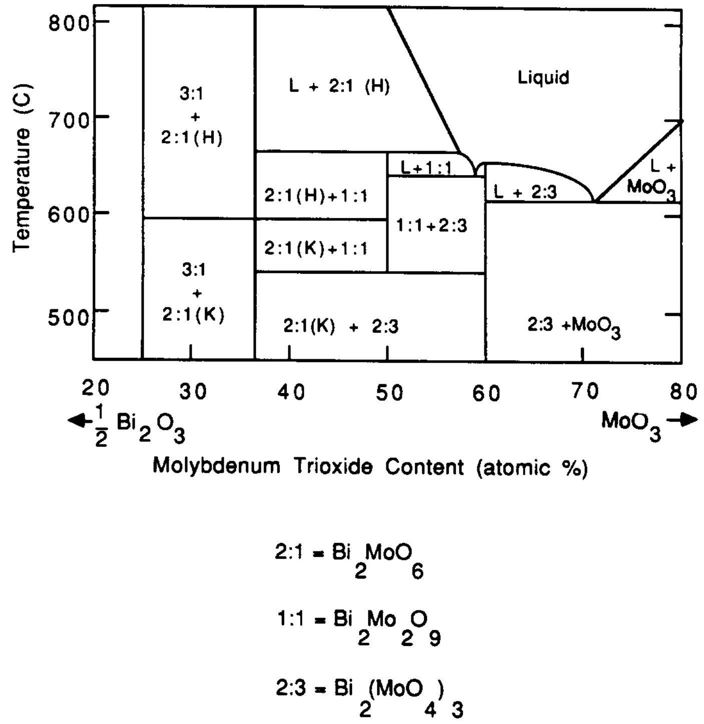

FIG. 2. Phase diagram for the bismuth molybdate system adapted from Egashira *et al.* (*17*).

of the sample. The importance of this history to the stability of beta bismuth molybdate is consistent with the results summarized in Table 2 and has been confirmed in the present investigation.

It is important to note that we observed different behaviors for beta bismuth molybdate samples which had different temperature histories, yet which appeared to be identical in terms of both Raman and X-ray diffraction analyses.

TABLE 1

Stoichiometric Compositions of the Solid Phases of Bismuth Molybdates

Phase	Stoichiometric composition	Bi/Mo Ratio
Alpha	$Bi_2(MoO_4)_3$	2:3
Beta	$Bi_2Mo_2O_9$	1:1
Gamma	Bi_2MoO_6	2:1

It is well known (*25*) that bismuth molybdates will catalyze partial oxidation reactions under anaerobic conditions. However, their activity under these conditions eventually declines due to the loss of lattice oxygen. The involvement of lattice oxygen in the oxidation reaction has led many researchers to postulate that the surface and/or bulk of the catalyst may undergo rearrangement under reaction conditions. For instance, a beta bismuth molybdate surface may form on the exterior of even slightly nonstoichiometric alpha or gamma bismuth molybdates (*26*). This surface beta layer may be present only under reaction conditions (*27*). The surface layer may not even be beta bismuth molybdate, but actually a mixture of the alpha and gamma phases (*22*) or of the gamma phase and MoO_2 (*24*) with an overall stoichiometry of Bi : Mo = 1 : 1.

The question of catalyst stability under reaction conditions is an extremely important one since the results of any study

TABLE 2

Summary of Literature Relevant to the Formation and Decomposition in Air of β-$Bi_2O_3(MoO_3)_2$ from Fresh Bi/Mo Co-precipitates and from Mixtures of α-$Bi_2O_3(MoO_3)_3$ and γ-$Bi_2O_3MoO_3$

Citation	Reactants	Treatment	Products/method of analysis (at ambient temperature)
Theobald *et al.* (*20*)	α-$Bi_2O_3(MoO_3)_3$ and γ-$Bi_2O_3MoO_3$ precipitated at pH 6–7, dried and ground	Gradually heated in air to 550°C in 50°C increments	β-$Bi_2O_3(MoO_3)_2$/ neutron diffraction
Batist *et al.* (*18, 19*)	Bi/Mo = 1; precipitate obtained at pH 1 and adjusted to pH 5 prior to filtration	Dried at 110°C, calcined for 2 hours at 550°C and 90 hr at 450°C	β-$Bi_2O_3(MoO_3)_2$ X-ray diffraction
Carson *et al.* (*22*)	Bi/Mo = 1; precipitate adjusted to pH 7 prior to evaporation of the liquid	Dried below 200°C and gradually heated in 50°C steps to 450°C with several hours at each step	α-$Bi_2O_3(MoO_3)_3$ and γ-$Bi_2O_3MoO_3$/infrared spectroscopy and X-ray diffraction
Carson *et al.* (*22*)	Bi/Mo = 1; precipitate adjusted to pH 7 prior to evaporation of the liquid	Further calcination between 600 and 650°C	β-$Bi_2O_3(MoO_3)_2$/infrared spectroscopy and X-ray diffraction
Gryzbowska *et al.* (*23*)	Bi/Mo = 1; precipitate obtained at pH 2 and filtered	Dried at 110°C and calcined for 11 hr at 400°C	β-$Bi_2O_3(MoO_3)_2$/ X-ray diffraction
Gryzbowska *et al.* (*23*)	Bi/Mo = 1; precipitate obtained at pH 2 and filtered	Further calcined at 400°C for a total of 16 hr or more at 400°C	α-$Bi_2O_3(MoO_3)_3$ and γ-$Bi_2O_3MoO_3$/X-ray diffraction
Gryzbowska *et al.* (*23*)	Bi/Mo = 1; precipitate obtained at pH 2 and filtered	Dried at 110°C and calcined at 550°C for 11 or 48 hr	β-$Bi_2O_3(MoO_3)_2$/ X-ray diffraction
Egashira *et al.* (*17*)	Bi/Mo = 1; precipitate adjusted to pH 7 prior to evaporation of the liquid	Calcined at 500°C	α-$Bi_2O_3(MoO_3)_3$ and γ-$Bi_2O_3MoO_3$/X-ray diffraction
Egashira *et al.* (*17*)	Bi/Mo = 1; precipitate adjusted to pH 7 prior to evaporation of the liquid	Further calcined at 580 and 650°C	β-$Bi_2O_3(MoO_3)_2$/ X-ray diffraction
Egashira *et al.* (*17*)	α-$Bi_2O_3(MoO_3)_3$ and γ-$Bi_2O_3MoO_3$ separately prepared by precipitation; followed by calcination at 500 to 650°C for 10 hr	Calcined at 543 to 594°C. Method of mixing/contacting not given	β-$Bi_2O_3(MoO_3)_2$ 95% complete after 15 hr at 594°C/X-ray diffraction
Egashira *et al.* (*17*)	β-$Bi_2O_3(MoO_3)_2$; preparation not clear; prior calcination above 540°C implied	Prolonged heating below 530°C	α-$Bi_2O_3(MoO_3)_3$ and γ-$Bi_2O_3MoO_3$/X-ray diffraction
Monnier and Keulks (*25*)	β-$Bi_2O_3(MoO_3)_2$; method of preparation not clear	Prolonged heating between 300 and 470°C	β-$Bi_2O_3(MoO_3)_2$/not given
Kumar and Ruckenstein (*24*)	β-$Bi_2O_3(MoO_3)_2$; 400 Angstrom film on silica	Heating at 400°C for 1 hr	MoO_2 + γ-$Bi_2O_3MoO_3$/ X-ray diffraction

concerning the kinetics and/or mechanism of olefin oxidation are valid only if one knows the nature of the catalyst actually present. Hence, one must be cognizant not only of the literature dealing with the stabilities of the various bismuth molybdates under the calcination conditions described above, but also of how these stabilities are related to phenomena occurring in the presence of reactive gases at elevated temperatures.

Stability of Alpha Bismuth Molybdates

Of the three bismuth molybdates of interest to researchers in catalysis, the alpha phase possesses the greatest thermal stability, melting at ca. 649°C and being completely stable below this temperature (*17,* *28*). There are many indications that this catalyst is also quite stable under reaction conditions. Many laboratories have concluded from *pre-* and *post-situ* studies of this catalyst that it is also stable under reaction conditions provided that sufficient oxygen is present in the feed gas (*29–35*). However, *in-situ* studies may provide an important contrast to this result.

Using *in situ* high resolution electron microscopy (HREM), Gai (*27*) has observed the formation of beta bismuth molybdate on an alpha phase catalyst during the aerobic partial oxidation of propylene. However, the beta phase observed under reaction conditions was not present when the catalyst was cooled (in air) to room temperature. During the cooling process this catalyst was transformed so that it again became a pure alpha bismuth molybdate. These observations indicate the possibility of reversible, dynamic changes in the catalyst under reaction conditions. One of the objectives of the present study was to study such changes *in situ* using Raman spectroscopy.

Stability of Beta Bismuth Molybdate

The thermodynamic stability of the beta phase has been investigated by several research groups. With the important exception of Keulks and co-workers (*25, 32*), most authors (*17–20, 22*) agree that the beta phase is stable from 540 to 660°C and metastable at room temperature.

Batist (*33*) reported that the beta phase is not only thermally unstable at typical reaction temperatures (320 to 450°C), but also is unstable under redox conditions. He observed the decomposition of a beta phase catalyst into alpha and gamma phases after 48 hr under reaction conditions. However, this decomposition did not have a major influence on the activity of the catalyst. Unfortunately, these conclusions may be subject to debate, as the report cited by Batist as the original source of the information given above (*36*) contains no information on the stability of the beta phase.

Kumar and Ruckenstein (*24*) studied the stability of the beta phase *in situ* using transmission electron microscopy. When their 400-Å thick beta bismuth molybdate film was heated in air at 425 to 500°C, the beta phase decomposed into gamma bismuth molybdate and MoO_2 within 30 min. Gai (*37*) also used electron microscopy to study the beta phase *in situ* during the aerobic and anaerobic partial oxidation of propylene at 400 to 440°C. During the anaerobic oxidation of propylene, she observed the decomposition of the catalyst into alpha bismuth oxide, molybdenum oxide, and bismuth metal. The addition of oxygen to the feed inhibited, but did not halt, the disintegration of the beta bismuth molybdate catalyst and prolonged its activity.

Brazdil *et al.*(*35*) reported that beta bismuth molybdate undergoes a very sharp decline in activity under even mildly reducing conditions. Data for the activation energies associated with reoxidation reactions of reduced forms of the various bismuth molybdate phases were interpreted in terms of a reductive disproportionation process in which the beta phase reacts to give slightly reduced forms of alpha and gamma bismuth molybdates, the alpha phase being present in the bulk of the reduced catalyst and the gamma phase on the surface. Reoxidation of the reduced beta catalyst below 540°C did not result in recombination of these phases, but rather in the formation of fully oxidized bulk alpha and surface gamma phases.

Further studies by Grasselli *et al.* using Raman spectroscopy (*38*) confirmed the disproportionation of the beta phase into alpha and gamma bismuth molybdates under reducing conditions. On the basis of these Raman studies, it was asserted that the presence of alpha and gamma bismuth molybdates in a beta phase catalyst will nucleate further disproportionation of the beta phase at 480°C. These workers further concluded that pure beta bismuth molybdate is thermally stable up to 600°C. This conclusion is contrary to results obtained by other investigators (*17, 23, 24*). However, a close reading of the paper in question indicates that what Grasselli *et al.* observed is not the thermal stability of pure beta bismuth molybdate "up to 600°C" but rather "at 600°C." The "nucleated" disproportionation of the beta phase at 480°C is interesting only if control experiments show that pure beta bismuth molybdate is stable at this temperature. No such control experiments were reported.

Thus, the preponderance of the experimental evidence indicates that beta bismuth molybdate is not stable under reaction conditions.

Stability of Gamma Bismuth Molybdate

The thermal stability of the gamma phase was the subject of a great deal of debate during the 1960's and early 1970's. Most authors now agree, however, that the gamma phase is metastable with respect to the gamma prime phase, although this transition occurs very slowly below 600°C (*15, 17, 19, 39–41*). The gamma phase is not mechanically stable and for this reason it is not used commercially (*42*).

Krenzke and Keulks (*31*) reported that their gamma bismuth molybdate exhibited no change in activity or selectivity during the aerobic partial oxidation of propylene below 460°C. Above this temperature the reaction became uncontrollable, resulting in an irreversible loss of catalytic activity. Batist *et al.* (*19*) observed a similar result during a study of butene isomerization. In contrast to the results of Keulks, however, Batist found that the activity of his deactivated catalyst could be restored by heating in a stream of oxygen. Further research by Batist and Lankhuijzen (*42*) demonstrated that gamma phase catalysts which have been partially reduced at 400°C will disproportionate into Bi_2O_3, bismuth metal, and MoO_3 due to the thermal instability of divalent bismuth:

$$3Bi^{2+} \rightarrow Bi\ (metal) + 2Bi^{3+}.$$

The catalyst structure can be restored by immediate reoxidation. However, if the sample is held at or above 400°C, bismuth atoms will migrate and agglomerate on a time scale of minutes. Subsequent reoxidation will then result in the formation of Bi_2O_3 clusters.

Brazdil *et al.* (*35*) also found that a partially reduced gamma bismuth molybdate could be restored to its initial activity, selectivity, and structure by reoxidation. Batist (*33*) reported that gamma bismuth molybdate catalysts used for the oxidative dehydrogenation of butene maintain their activity and selectivity for periods of a year or more provided that there is enough oxygen and that the temperature does not exceed 480°C. It is thus apparent that gamma bismuth molybdate is quite stable under reaction conditions.

Gai (*27*) has also studied the catalytic properties of gamma bismuth molybdates. As in her *in situ* studies of the alpha and beta phase catalysts, Gai noted the formation of beta bismuth molybdate on the gamma phase catalyst. This beta contaminant was present only under actual reaction conditions. The possibility of this "dynamic contamination" of the gamma phase has been investigated in the present study using *in situ* Raman spectroscopy. Similar studies concerning the alpha and beta phases have also been carried out.

EXPERIMENTAL

Laser Raman System

The Raman spectrometer was a Spex Ramalog 5 (Model 14018) system equipped with a third monochrometer to resolve weak bands near the exciting line. The monochromatic light source was a Spectra Physics Model 164 argon ion laser powered by a Spectra Physics Model 265 exciter. The spectrometer was interfaced with a DEC PDP-11/03-LC minicomputer system to facilitate data acquisition and manipulation. All spectra were recorded using the 488.0 nm line of the argon laser for excitation. A rotating lens assembly was used to minimize sample degradation due to localized heating

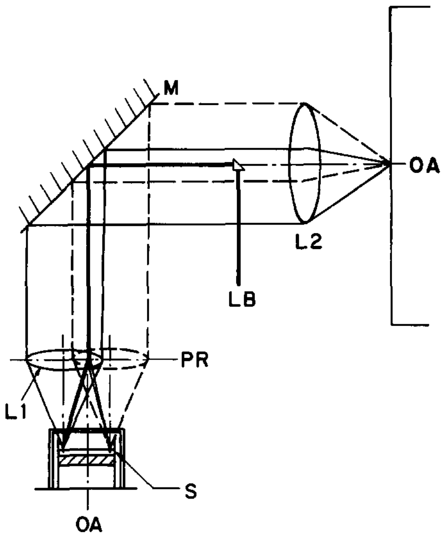

FIG. 3. Rotating lens system after Zimmerer and Kiefer (*45*). LB: laser beam; OA: optical axis; M: plane mirror; L1: condenser lens; L2: telescope lens; S: sample surface; PR: plane of rotation.

of the catalyst sample by the laser beam. This assembly is of the general type described by Zimmerer and Kiefer (43). A schematic diagram of the assembly is shown in Fig. 3.

A column of laser light (LB) is directed away from the spectrometer along the optical axis (OA) by a prism. The light is then deflected downward by a plane mirror (M). A condenser lens (L1, 1.5 in., f/1.3 plano-convex) then focuses the light at a point on the sample which is directly behind the center of the lens. The condenser lens is mounted so that it can be rotated (1000 rpm); however, the center of the lens is displaced from the axis of rotation. As this assembly is rotated about the optical axis of the spectrometer, the focal point of the condenser lens moves in a circle, and thus the focused laser beam moves over the sample surface (S) in a circle.

The light that is scattered by the catalyst surface is collected and collimated by the condenser lens (L1). The scattered light is then directed back toward the spectrometer by the mirror (M). This column of light is then focused on the spectrometer slit by a telescope lens (L2). Because the scattered light is collimated by the condenser lens, the telescope lens focuses the light to a point which remains stationary on the spectrometer slit. Thus, the observed intensity of the scattered light remains constant as the condenser lens is rotated.

Additional details concerning the Raman system employed have been discussed by Kovats (*44*), Kovats and Hill (*45*), and Wilson (*46, 47*). Spectra may be obtained from samples in controlled atmospheres at elevated temperatures and under *in situ* conditions in a flow reactor as well as at ambient conditions. The Raman spectra reported in this paper were typically recorded at a resolution of 5 cm^{-1} (slit width 365 μm, slit height 20 nm), a laser power of 200 mW for the 488 nm line of argon, and a step size of 1.5 cm^{-1}/datum. The collection times and number of scans were adjusted as appropriate to obtain high quality spectra.

Reactor and in Situ Cell

The gas handling system used in this investigation contained provisions for feeding oxygen, propylene and helium through appropriate regulators at 25 to 40 psig to individual Tylan (Carson, CA) mass flow control valves. After passing through the flow control valves the gases were mixed and fed to a six-way, two-position valve. This valve was used to select one of two flow patterns. In the first pattern, the feed was directed through the gas chromatograph and subsequently to the reactor. In the second pattern, the gas mixture was fed directly to the reactor and the effluent from the reactor was directed to the gas chromatograph. Additional information concerning this reactor is presented elsewhere (*48*).

The reactor cell used for *in situ* Raman examination of the bismuth molybdate catalysts is shown schematically in Fig. 4. Several criteria were established for the design of this cell. The most important criterion was that the cell have a window through which the catalyst could be exposed to the

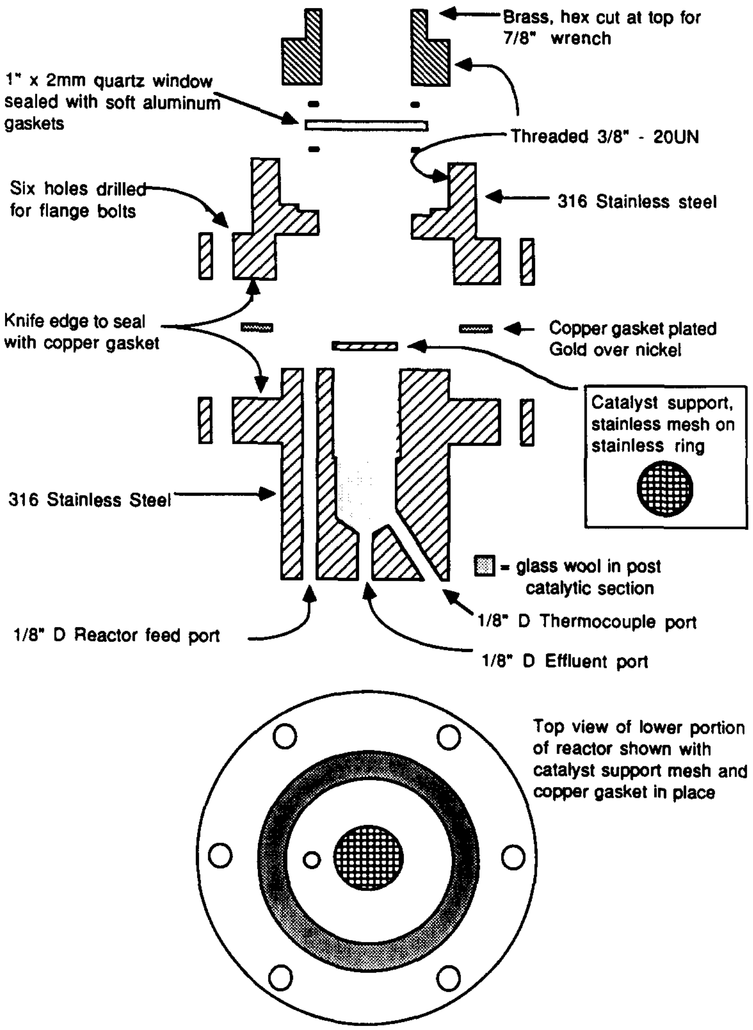

FIG. 4. Schematic diagram of reactor cell used to conduct *in situ* Raman studies of catalysts.

incident laser beam. Moreover, the reactor must not have a large dead volume. Preliminary calculations showed that the reactor should hold about 2 cc of catalyst in order to achieve propylene conversion levels which could be easily measured. Since several different catalysts were examined, the reactor was designed for easy access to the catalyst. The window was fabricated as a separate unit so that, once established, the seal on the window need not be broken in order to access the catalyst. The gaskets on either side of the window needed to be soft enough to form a seal without breaking the pyrex glass and yet still withstand reaction temperatures. Since copper oxide is known to catalyze the partial oxidation of propylene, the copper gaskets were electroplated, first with nickel, and then with gold. The thermocouple was located as close as possible to the catalyst bed to facilitate accurate determination of the temperature. Additional information relative to the *in situ* reactor/Raman sample cell is presented elsewhere (*48*).

Preparation of Bismuth Molybdates

The bismuth and molybdenum reagents used in these preparations were gravimetrically analyzed for metal content by calcination to either Bi_2O_3 or MoO_3. Specific preparations are described below.

ALPHA01. A bismuth solution was prepared by adding 0.0600 moles of bismuth nitrate, Fisher lot #755322, to 30 ml concentrated HNO_3 and then diluting to 1200 ml with water. A molybdenum solution was prepared by adding 0.0940 moles of molybdenum as J. T. Baker lot #1757 ammonium molybdate to 200 ml water and adjusting the pH to 1.5 with HNO_3. These solutions were allowed to age overnight before dropwise addition of the bismuth solution to the molybdenum solution over the course of 3 hr. The pH was maintained at 1.5 throughout this process by addition of ammonium hydroxide. The resultant precipitate was filtered, dried overnight at 145°C, and then calcined at 200°C for 4 hr and at 520°C for 20 hr. Raman analysis indicated that the compound was alpha bismuth molybdate containing traces of MoO_3. ICP analysis indicated a 2.2% excess of molybdenum over stoichiometric alpha bismuth molybdate.

BETA01. First, 0.0200 moles of $Bi(NO_3)_3 \cdot 5H_2O$, Aldrich lot #01322CK, were added to 10 ml of 15.6 *M* HNO_3. This mixture was stirred and diluted with 150 ml water over the course of 2 min. Then, 0.0200 moles of molybdenum in the form of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, Mallinkrodt lot #KAMC, were dissolved in 100 ml water. This solution was adjusted to pH 1.8 using HNO_3 and allowed to age for 1 hr prior to mixing. At 25°C the bismuth solution was added to the molybdenum solution dropwise over the course of 1 hr. During this process, the pH was controlled at 1.8 via computer controlled addition of 10% ammonium hydroxide. The slurry formed during mixing was aged at 25°C, pH 1.8 for 3 hr before filtering. The filter cake was dried at 190°C for 24 hr to remove any residual ammonium nitrate. The filter cake was then calcined at 561°C for 24 hr. Raman spectra of the product revealed only the presence of beta bismuth molybdate within the limits of detectability (0.5%). This sample was not contaminated by either the alpha or gamma phases.

BETA02. This sample preparation was based on the method given by Gryzbowska *et al.* (*23*) for the preparation of beta bismuth molybdate. Two solutions were prepared. The first contained 0.0100 moles of bismuth as Fischer lot #755322 $Bi(NO_3)_3 \cdot 5H_2O$ dissolved in 5 ml of 15.6 molar HNO_3 and subsequently diluted with 25 ml of water. The second contained 0.0100 moles of molybdenum as CCL lot #230906 $(NH_4)_6Mo_7O_{24}$ dissolved in 100 ml of water and adjusted to pH 2 with HNO_3. The bismuth solution was added dropwise to the molybdenum solution at a controlled temperature of 25°C over a period of 40 min with constant stirring. During mixing the pH of the solution was maintained at 2.00 ± 0.07 via computer controlled addition of 5% (vol) ammonium hydroxide. The resulting pale yellow precipitate was aged in the mother liquor at pH 2.00 for 30 min before filtration. The filter cake was not washed before calcination at 400°C for 2 hr. ICP examination of the pale yellow product indicated a bismuth-to-molybdenum mole ratio of 1.02. Quantitative Raman analysis indicated that the product contained 7.6% alpha, 92.0% beta, and 0.4% gamma bismuth molybdate.

GAMMA01. This compound was prepared following the method given by Carson *et al.* (*22*). A solution of 0.0100 moles molybdenum as ammonium molybdate, CCL lot #230906, in 15 ml 5% NH_4OH(pH 7.0) was added dropwise to a solution of 0.0200 moles bismuth nitrate, Aldrich lot #01322CK, in 50 ml 5.0 *M* HNO_3 at 25°C. The final pH was adjusted to 7.0 using ammonium hydroxide. The white precipitate and mother liquor were heated to 450°C over a period of several hours. Raman analysis indicated that the product was gamma bismuth molybdate containing traces ($<1\%$) of beta bismuth molybdate.

MIX01. This preparation was adapted from the method given by Batist (*49*) for preparation of alpha bismuth molybdate. The molybdic acid used in this preparation, BDH lot #4717780G, contained 95.08% molybdenum as MoO_3. This level was much greater than the expected value of 85%, or the value of 88.3% reported by Batist for another lot of this product.

First, 0.005 moles bismuth as Sigma lot #113F-0223 bismuth oxynitrate were added directly to 100 ml of water containing 0.015 moles of molybdenum as molybdic acid. Thus, a factor of two excess of molybdenum was used relative to the formation of stoichiometric $Bi_2(MoO_4)_3$. (Batist recommends a factor of six excess.) The slurry was then boiled for 30 hr with reflux. After 2 hr of boiling, the slurry turned a light yellow green color. After 30 hr, its color was light yellow. The precipitate was dried, calcined at 490°C for 2 hr, powdered, filtered with 200 ml of 30% ammonium hydroxide, and finally calcined at 490°C for 1 hr. Raman analysis of the product indicated the presence of 20.5% alpha, 66.3% beta, and 13.2% gamma bismuth molybdate.

RESULTS AND DISCUSSION

Three sets of experiments were carried out to assess the effects of temperature and environmental composition on the stability of the three catalytically active bismuth molybdate phases. Samples were examined before and after various calcination treatments in stagnant air and *in situ,* both when subjected to heating in a stream of air and when exposed to conditions under which the partial oxidation of propylene to acrolein occurs rapidly. The results of each set of experiments are discussed in the subsections which follow. First, however, it is necessary to indicate why we conducted two types of calcination experiments (stagnant and flow).

Most authors who have studied the thermodynamic stability of bismuth molybdates have done so by calcining the catalysts at various temperatures in stagnant air, cooling the samples to room temperature, and then determining the phase composition of the product using X-ray diffraction. We anticipated that results obtained from studies on catalysts heated in stagnant air should be entirely comparable to those studies performed on catalysts heated in flowing air. The flowing "air" mixture actually consisted of 20% oxygen in helium at a space velocity of 25 min^{-1} (STP). While we were most concerned with the results obtained *in situ* in flowing air, it was felt that there would still be some question as to whether these results would be comparable to those obtained in stagnant air. Because of this possibility and the fact that significant controversy surrounds the bismuth molybdate phase diagram, it was felt that both sets of circumstances warranted investigation. Control experiments performed in air at room temperature on mechanical mixtures of pure bismuth molybdates indicated that at room temperature the presence of a 2% change in the phase composition of a bismuth molybdate sample could be reliably detected. For the *in situ* studies at 400 to 500°C, a change of 5% in the phase composition could be detected.

Calcination in Stagnant Air

Four different samples were used to investigate the thermodynamic stability of the beta bismuth molybdate phase: BETA01, BETA02, MIX01, and a mechanical mixture consisting of equimolar amounts of the alpha and gamma phases (MIX02). Sample BETA01 contains only beta bismuth molybdate. BETA02 is an exact replicate of a beta phase preparation for which disproportionation was reported. (However, our analyses indicate that this sample also contains some alpha bismuth molybdate.) Sample MIX01 contains significant amounts of all three phases. These samples were examined before and after various calcination treatments in stagnant air. The reaction on which this study was focused can be written as

$$2\,Bi_2Mo_2O_9 \leftrightarrow Bi_2(MoO_4)_3 + Bi_2MoO_6. \quad (1)$$

If one starts with compounds located at both extremes of the equilibrium position as well as at an intermediate stage, it should be possible to detect whether either side of Eq. (1) is strongly favored at a particular temper-

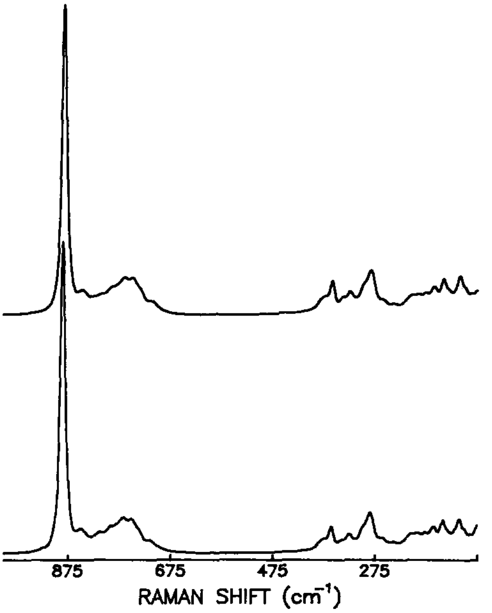

FIG. 5. Raman spectra of a pure beta bismuth molybdate obtained before (upper spectrum) and after (lower spectrum) calcination at 500°C for 5 days.

ature, presuming that the reactions of interest occur at appreciable rates.

The wet precipitate which was the precursor to BETA01 was calcined at 561°C for 25 hr. (For systems of the indicated starting compositions, this temperature lies within the region of thermodynamic stability for the beta phase reported in the literature.) The Raman spectrum of the calcined precipitate indicated only the presence of the beta bismuth molybdate.

A portion of this sample was further calcined at 500°C for five days in an attempt to observe the disproportionation reaction indicated above. The room-temperature Raman spectra obtained from this sample before and after heating at 500°C are shown in Figure 5. An increase in the intensity of the Raman signal at 900 or 791 cm^{-1} would indicate increases in the amounts of the alpha and gamma phases present, respectively. However, there were no detectable differences between the Raman spectra of this sample taken before and after calcination at 500°C. The control experiments noted earlier indicated that a 2% difference in phase composition could have been detected. Hence, this result indicates that disproportionation did not occur to a significant extent under these conditions.

To investigate whether or not the reverse of the reaction shown in Eq. (1) might be favored in this temperature range, an experiment was carried out using an intimate mechanical mixture of the alpha and gamma phases as the starting material (MIX02). This mixture consisted of equimolar amounts of pure alpha and gamma phases. These phases were ground to a fine paste with a small amount of water. This paste was dried at 110°C. After drying, the mixture was again ground to a fine paste, dried, and then ground to 80–120 mesh. This sample was calcined at 400°C for 70 hr and then further calcined at 460°C for 48 hr. Room temperature Raman spectra were obtained after calcination at 400°C and after calcination at 460°C. Comparison of these spectra with that of the uncalcined sample provided no indication that these two phases had reacted to form the beta phase.

A careful reading of the papers of various authors who had reported decomposition of the beta phase at reaction temperatures revealed the possibility that the properties of a beta phase catalyst which had been calcined above 540°C might be different than those of a catalyst which had been calcined below this temperature. The paper generally cited as providing evidence for the lack of stability of beta phase catalysts at 400°C is that of Gryzbowska *et al.* (*23*). Consequently, we prepared a beta phase sample (BETA02) using the procedure described by these researchers. In this preparation protocol the precipitate is calcined for 2 hr at 400°C. Using X-ray diffraction, Gryzbowska *et al.* found that this compound showed some signs of decomposition after 16 hr of calcination at 400°C. After 48 hours there was a very clear indication that the compound was decomposing into alpha and gamma phases. We attempted to duplicate this result by fur-

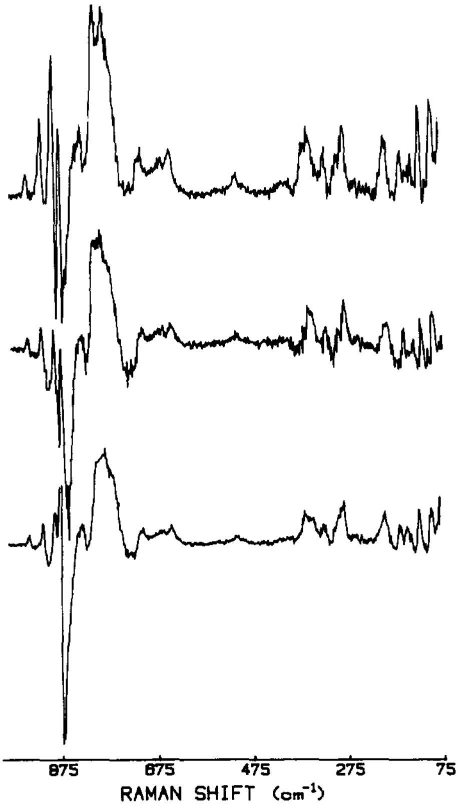

FIG. 6. Spectra obtained by subtracting the Raman spectrum of sample BETA02 obtained after calcination at 400°C for 2 hr from spectra obtained after calcination for 43 hr (lower spectrum), 89 hr (middle spectrum), and 123 hr (upper spectrum).

ther calcination of our sample (BETA02) for 17 hr at 400°C. This sample had previously been calcined for only 2 hr at 400°C. The room temperature spectrum obtained after this treatment was carefully compared to that of the sample which had been calcined for only 2 hr. There were no detectable differences between these two spectra. The sample was then calcined further at 400°C, and room temperature spectra were obtained after 43, 89, 125, 195, and 267 hr of calcination at 400°C.

The spectra obtained by subtracting the spectrum of the sample obtained after only 2 hr of calcination from the spectra obtained after further calcination at 400°C are shown in Fig. 6. In these difference spectra, the presence of positive peaks at 899, 924, and 954 cm^{-1} are indicative of an increase in the amount of alpha bismuth molybdate present in the sample. Positive peaks at 279, 358, and 792 cm^{-1} indicate an increase in the amount of gamma bismuth molybdate present. Negative peaks at these wave numbers would indicate decreases in the amounts of these phases present. The difference spectra in Fig. 6 clearly indicate increases in the amounts of the alpha and gamma phases present in sample BETA02 after calcination at 400°C for 43 hr relative to the amounts present after only 2 hr at this temperature. After 89 and 125 hr of calcination at 400°C, the presence of the alpha and gamma phases is still detectable only by examination of the difference spectra. The Raman spectra obtained after 2, 195, and 267 hr of calcination at this temperature are shown in Fig. 7. In these conventional spectra the growth with time of the amount of alpha bismuth molybdate present in this sample (peaks at 899, 924, and 954 cm^{-1}) is very easy to dis-

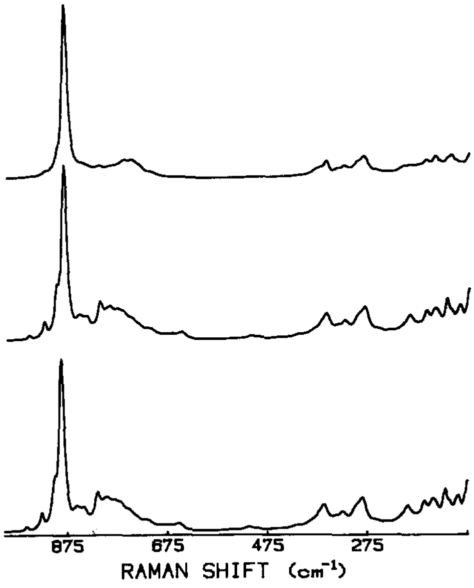

FIG. 7. Raman spectra of beta bismuth molybdate sample BETA02 after calcination at 400°C for 2 hr (upper spectrum), 195 hr (middle spectrum), and 267 hr (lower spectrum).

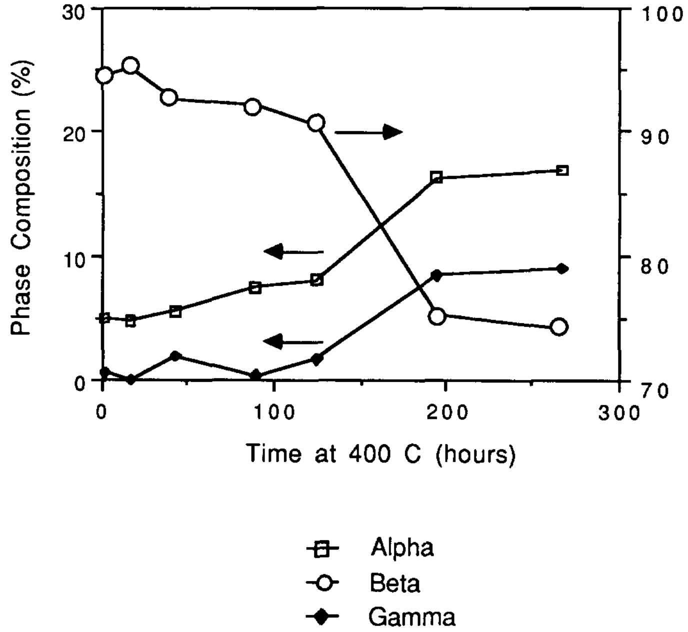

FIG. 8. Phase composition of a beta bismuth molybdate (sample BETA02) as a function of the time of calcination at 400°C.

cern. Peaks at 279, 358, and 792 cm^{-1} likewise indicate a significant increase in the amount of gamma bismuth molybdate present in this sample. Quantitative analysis of these spectra permit one to determine the phase composition of this sample as a function of the time of calcination at 400°C. These results are presented in Fig. 8. Note that more than a week is required to achieve an approach to equilibrium and that when the beta phase is prepared in the manner described for sample BETA02 (only 2 hr of calcination at 400°C), it is indeed unstable at this temperature. This result indicates that disproportionation of the beta phase occurs not only under reducing conditions as reported by Grasselli *et al.* (*38*), but also in an oxidizing atmosphere, provided that the sample has never been calcined above 500°C.

In an effort to confirm a claim in the literature (*38*) that the presence of alpha and gamma phases in a beta phase catalyst will "nucleate" disproportionation of the beta phase, Raman spectra were obtained from a sample (MIX01) containing all three phases (21% alpha, 66% beta, and 13% gamma). This sample was obtained from a coprecipitation process. Consequently, we believe that the three phases are well mixed on a microscale. The highly intimate nature of the various phase contacts should eliminate the possibility that reaction would not be observed simply for reasons of inadequate mixing of the phases. Room temperature Raman spectra of the sample were obtained both after calcination of the precipitate for 3 hr at 490°C and after calcination at 500°C for 5 days. These spectra indicate that no changes in the phase composition of this sample occurred during calcination at 500°C.

In Situ Examination of Catalysts Heated in Air

The stability of bismuth molybdate catalysts heated in flowing artificial air (20% oxygen in helium) was investigated as a precursor to investigations which would involve their use for the partial oxidation of propyl-

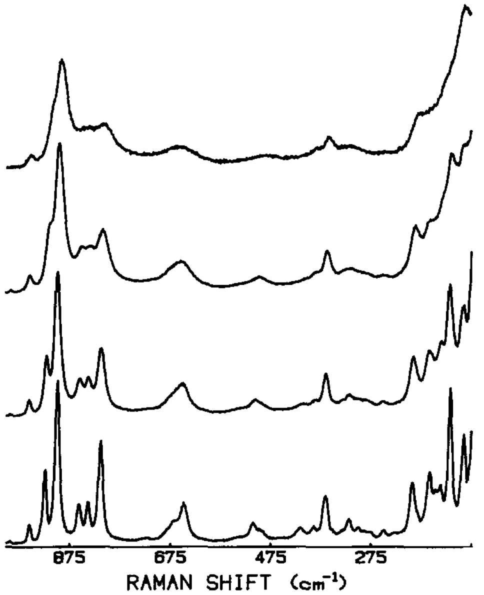

FIG. 9. Raman spectra of alpha bismuth molybdate (sample ALPHA01) obtained *in situ* at temperatures up to 600°C. From bottom to top: 25, 200, 400, 600°C.

ene. The space velocity employed was 25 min^{-1} for the gases at STP.

A sample of alpha bismuth molybdate containing less than 1% molybdenum trioxide [ALPHA01] was heated to 600°C in 100°C steps over a period of 24 hr. Raman spectra obtained *in situ* during this process are shown in Fig. 9. As the temperature of this sample was raised, the peaks in these spectra broadened and there was an overall loss of signal intensity. However, in accordance with the theory of the Raman effect (*50*), the peak positions did not shift. There is no indication in Fig. 9 of any change in the phase composition of this sample during heating. A spectrum of this sample recorded after the calcined sample was cooled to room temperature was identical to that of the fresh sample.

Because of the widely reported thermodynamic instability of beta bismuth molybdate, the experiments performed on samples of BETA01, a pure beta phase compound, were of particular interest. A sample of this material was held in flowing artificial air at 500°C for 12 days. While the sample was held at 500°C, Raman spectra were collected *in situ* after 1, 3, 6, 48, 90, 216, and 288 hr. All of these spectra are identical. The spectra taken at 500°C are shown in Fig. 10. After treatment at 500°C, the temperature was lowered to 400°C, which is more typical of the temperatures used for the partial oxidation of propylene. Spectra of this sample were taken after 1 hr and after 30 days at this temperature. No change in the phase composition of this sample was evident in a thorough inspection of these spectra. Raman spectra obtained after cooling the sample to room temperature were identical to those of the fresh sample.

Since Raman spectroscopy is relatively surface sensitive, samples of the beta phase materials were subjected to grinding to assess whether changes in the bulk composition of a catalyst might have taken place during calcination. Grinding the compound reveals the bulk for Raman analysis. Any changes in spectra taken before and after grinding would then be indicative of surface/

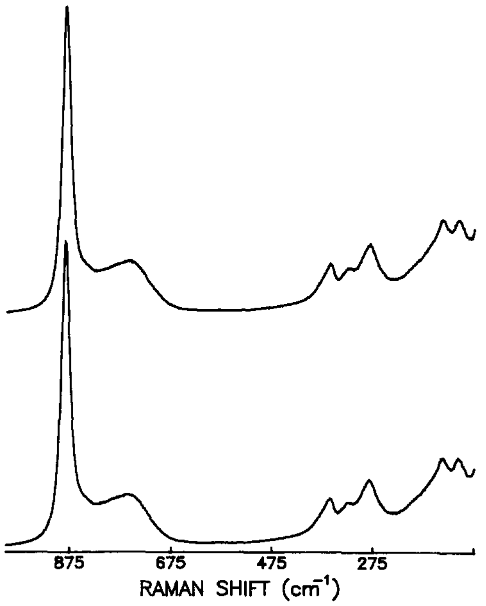

FIG. 10. Raman spectra of pure beta bismuth molybdate (sample BETA01) obtained *in situ* after 1 hr (upper spectrum) and after 12 days (lower spectrum) at 500°C.

TABLE 3

X-ray Diffraction Patterns for Pure Beta Bismuth Molybdate, Sample BETA01

(1) Fresh catalyst		(2) After calcination	
d (Å)	Intensity	*d* (Å)	Intensity
7.94	2	7.97	2
6.60	6	6.62	6
5.91	7	5.93	4
5.18	4	5.19	4
4.89	9	4.90	10
4.76	6	4.77	6
3.91	2	3.92	2
3.77	4	3.77	4
3.30	2	3.30	2
3.19	100	3.20	100
3.15	10	3.15	14
2.98	2	2.98	2
2.80	29	2.81	29
2.73	2	2.74	3
2.69	15	2.70	15
2.19	4	2.19	4
2.17	4	2.18	4
1.99	8	1.99	9
1.98	9	1.98	9
1.95	32	1.95	32
1.92	3	1.92	3
1.69	20	1.69	20
1.64	15	1.64	15
1.63	10	1.63	10
1.60	8	1.60	8

Note. (1) Fresh sample as prepared, (2) after heating for 12 days at 500°C and then for 30 days at 400°C.

bulk inhomogeneities. However, in the present case there were no detectable differences in these spectra. X-ray diffraction patterns of this catalyst were obtained before and after the aforementioned treatment (288 hr at 500°C and 30 days at 400°C). This procedure was thought to be advisable, since most authors use X-ray diffraction to determine the phase compositions of their catalysts. These X-ray patterns are given in Table 3. There is no evidence of any significant difference between the patterns of the fresh and the heat treated samples.

A gamma bismuth molybdate catalyst (GAMMA01) was heated for 24 hr at 400°C. Raman spectra of this catalyst obtained *in situ* after 1 hr and after 24 hr at this temperature are shown in Fig. 11. There are no significant differences between these spectra. This result confirms the conclusion of other authors (*17*) that the gamma phase is stable at this temperature.

The stability of sample MIX01 containing 21% alpha, 66% beta, and 13% gamma bismuth molybdate was also investigated. This sample was exposed to the flowing mixture of oxygen (20%) and helium for 26 days. Raman spectra were obtained *in situ* after 2 hr and after 26 days at 400°C. These spectra indicated that no detectable change occurred in the phase composition of this catalyst during this period of time. Control experiments using mechanical mixtures of the pure phases indicated that a change as small as 5% in phase composition could easily have been detected.

In Situ Examination under Reaction Conditions

The final set of experiments dealt with the stabilities of the various bismuth molybdate

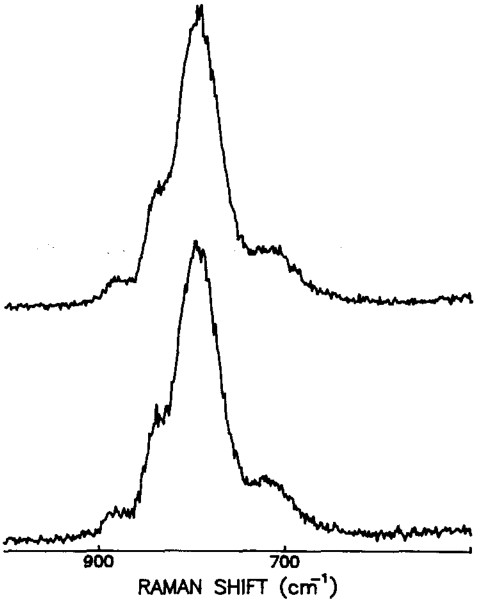

FIG. 11. Raman spectra of gamma bismuth molybdate (GAMMA01) at 400°C. Upper spectrum after 1 hr, lower spectrum, after 24 hr.

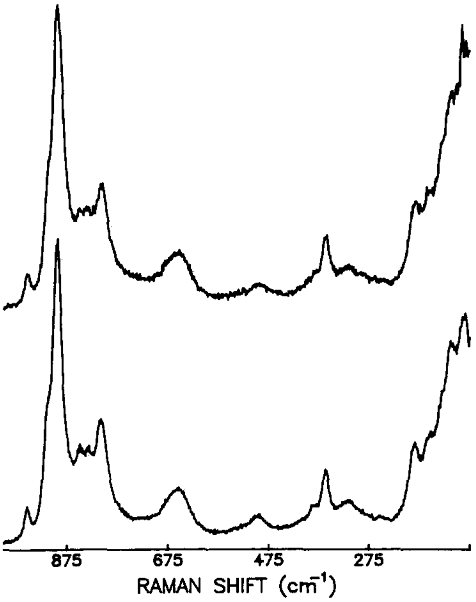

FIG. 12. Raman spectra of alpha bismuth molybdate (ALPHA01) obtained *in situ* after 1 hr (upper spectrum) and after 24 hr (lower spectrum) of use for the partial oxidation of propylene at 400°C.

phases under reaction conditions. Several catalyst samples were exposed at elevated temperatures to a gas mixture consisting of 20% oxygen and 10% propylene in helium at a space velocity of 25 min^{-1} (STP). Raman spectra were recorded *in situ* to determine whether any phase changes were induced by exposure of these catalysts to the reacting gas mixture.

This set of experiments was designed to address the question of whether exposure of these catalysts to reaction conditions induces any reversible phase changes which could be detected by *in situ* studies, but which would not be evident in conventional room temperature analyses of these samples. Monophasic samples of alpha, beta, and gamma bismuth molybdate were taken from preparations ALPHA01, BETA01, and GAMMA01, respectively. In addition to these compounds, the mixed phase sample MIX01 was studied. Each of these four samples was heated to 400°C in the flowing reaction gas mixture. The activity and selectivity of each catalyst were measured periodically throughout each test using gas chromatography for analysis of the effluent gases. Typical conversion levels were 20–40%. Selectivities to acrolein were 50–90% based on the propylene reacted. No significant changes (>7%) in the activity or selectivity of any catalyst sample were noticed during a 24-hr test period.

The Raman spectra of these samples taken after 1 hr and after 24 hr of use for the partial oxidation of propylene are shown in Figs. 12–15. Examination of these *in situ* spectra revealed no changes in the phase compositions of any of these samples during this time. The spectra of these catalysts obtained after 24 hr in the reaction gas mixture were also compared to those obtained in a flowing mixture of 20% O_2 and 80% helium. These comparisons revealed no detectable differences between the catalyst held in air and those exposed to the reaction mixture. For the *in situ* Raman spectra obtained from samples at 400°C, the control experiments

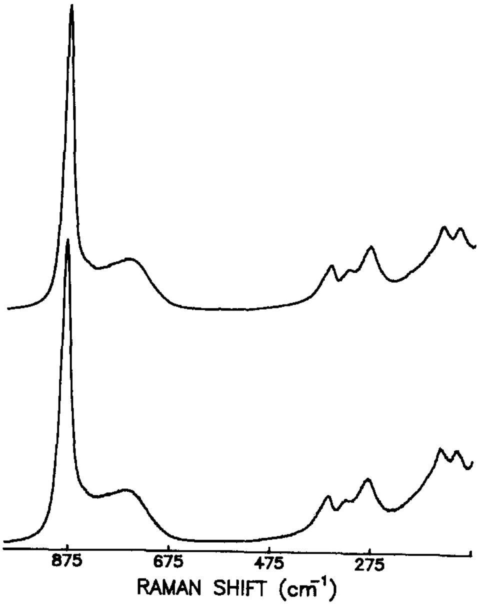

FIG. 13. Raman spectra of beta bismuth molybdate (BETA01) obtained *in situ* after 1 hr (upper spectrum) and after 24 hr (lower spectrum) of use for the partial oxidation of propylene at 400°C.

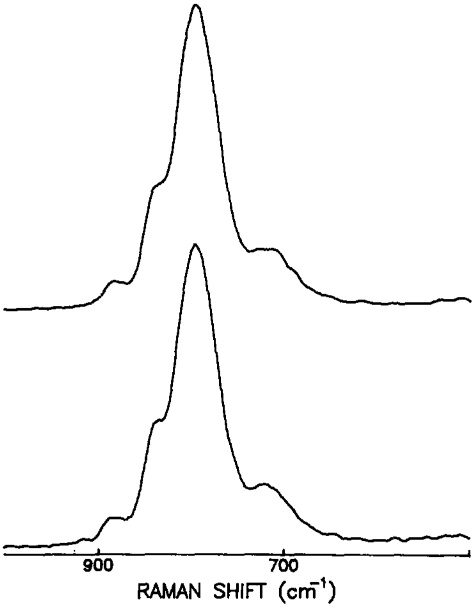

FIG. 14. Raman spectra of gamma bismuth molybdate (GAMMA01) obtained *in situ* after 1 hr (upper spectrum) and after 24 hr (lower spectrum) of use for the partial oxidation of propylene at 400°C.

indicated that a change in phase composition of as little as 5% could have been detected. At room temperature, a change of 2% in phase composition could easily have been found. No changes, reversible or irreversible, were apparently caused by the use of these catalysts for the partial oxidation of propylene at 400°C. So far as we are aware, this study is the first to obtain quantitative information on the phase compositions of these catalysts *in situ* at temperatures and reactant pressures normally used for the catalytic partial oxidation of propylene.

SUMMARY OF RESULTS

The most significant experimental results may be summarized as follows:

1. A sample of beta bismuth molybdate [BETA01] was prepared via a coprecipitation technique and calcination at 561°C for 24 hr. Raman and X-ray diffraction data indicated that the resultant sample consisted solely of the beta phase. This material was subsequently calcined at 500°C for 12 days and then at 400°C for 30 days. Raman spectra obtained *in situ* revealed no changes in the phase composition of this compound at any point during this treatment. Raman spectra and X-ray diffraction patterns of this sample obtained at room temperature before and after this treatment are virtually identical.

2. A bismuth molybdate sample (BETA02) was prepared via a coprecipitation technique and calcined at 400°C for 2 hr. The Raman spectrum of this sample indicated that it contained 92% beta and 8% alpha bismuth molybdate. After the initial calcination at 400°C for 2 hr, this sample was held at 400°C for 43 hr. Careful scrutiny of the Raman spectrum obtained after this treatment revealed signs of increases in the amounts of the alpha and gamma phases present in this sample. After 267 hr at 400°C, Raman analysis indicated that this sample contained 17% alpha, 74% beta, and 9% gamma bismuth molybdate.

3. A mixture of bismuth molybdate phases

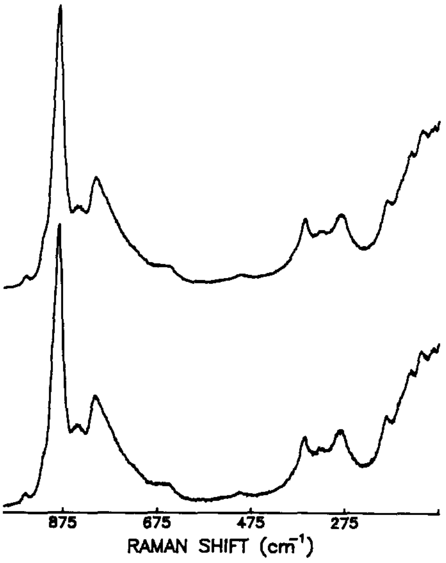

FIG. 15. Raman spectra of a mixed phase bismuth molybdate catalyst (MIX01) obtained *in situ* after 1 hr (upper spectrum) and after 24 hr (lower spectrum) of use for the partial oxidation of propylene at 400°C.

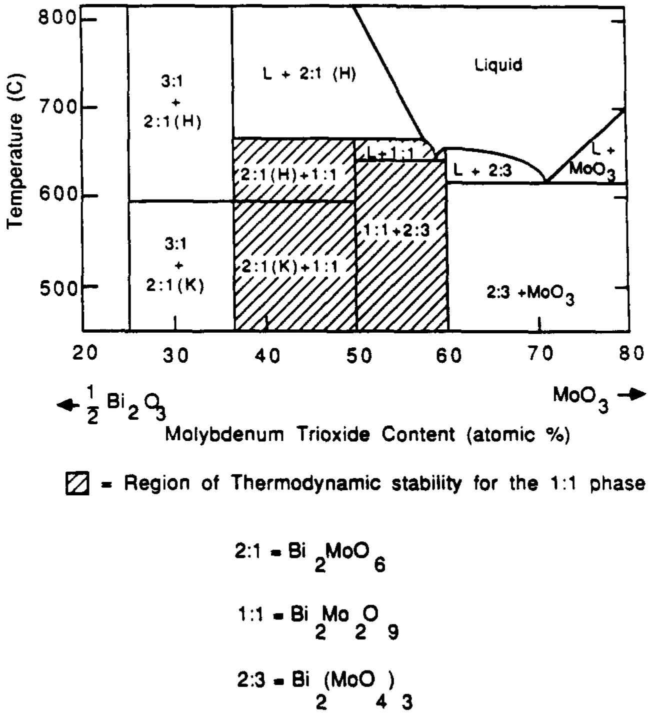

FIG. 16. The catalytically active region of the bismuth molybdate phase diagram. This diagram is the phase diagram given by Egashira *et al.* (*17*) modified to reflect the result that after appropriate annealing the beta phase is stable from room temperature to the melting point of this phase.

(MIX01) was prepared via a coprecipitation technique and calcined at 490°C for 3 hr. The Raman spectrum of this sample indicated the presence of 21% alpha, 66% beta, and 13% gamma bismuth molybdate. No changes were seen in the Raman spectra of this sample after subsequent calcination at either 500°C for 5 days or 400°C for 26 days.

4. The phase diagram for the bismuth molybdate system reported by Egashira *et al.* (*17*) should be modified to reflect the findings of the present research relative to the stabilities of the various phases. In particular, it should be noted that, when properly annealed, the beta phase is stable from room temperature to its melting point (see Fig. 16).

CONCLUSIONS

1. Beta bismuth molybdate which has been calcined at a sufficiently high temperature will not disproportionate on further heating at 400 to 500°C. The results of this study indicate that this critical temperature lies between 500 and 561°C.

2. Beta bismuth molybdate which has been calcined at 400°C will disproportionate into alpha and gamma phases on further heating at this temperature.

3. Some phenomenon other than the presence of small amounts of the alpha and gamma phases is responsible for the thermodynamic instability of beta phase compounds. The differences between the thermodynamic stabilities of beta phases noted above are most easily accounted for by differences in the thermal treatments to which they were subjected. These differences are not revealed in analyses by Raman spectroscopy and X-ray diffraction.

4. It is entirely possible to prepare alpha, beta, and gamma bismuth molybdate com-

pounds which are thermodynamically stable in air at 400 to 500°C. The thermal stabilities of these phases are not dependent on their purity, but rather on the temperature at which they have been calcined prior to being held at 400 to 500°C.

5. The *in situ* Raman studies indicate that properly annealed bismuth molybdates are not susceptible to phase changes when exposed to conditions typical of those employed for the partial oxidation of propylene to acrolein.

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