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The Chemistry of Bi-Mo Oxide Catalysts

I. Phase Composition of Catalysts and its Relation to the Structure of Precursors

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The effect of the conditions of preparation and thermal treatment on the phase composition of Bi-Mo oxide catalysts at the atomic ratio Bi/Mo = 1/1 has been studied. It has been shown that bismuth molybdate of the composition $Bi_2O_3 \cdot 2MoO_3$ (β-phase) is formed on crystallization of the precipitate prepared from appropriate salts at pH = 2 without additional reactions in the solid state. In the case of precipitation at pH = 7 and subsequent filtering, the calcined catalysts contained $Bi_2O_3 \cdot MoO_3$ (γ-phase). The precursor formed in these conditions was identical to the precipitate obtained by treating the precursor of the β-phase with concentrated aqueous ammonia, which led to dissolution of half of the molybdenum present in the sample. Comparison of ir spectra leads to the conclusion that the β-phase precursor is composed of layers of $[MoO_6]$ octahedra and $[MoO_4]$ tetrahedra, the latter being dissolved on ammonia treatment leaving $[MoO_6]$ octahedra as the precursor of the γ-phase (koechlinite). Catalysts obtained by precipitation at pH = 7 and subsequent evaporation are composed of a mixture of γ- and α-phase ($Bi_2O_3 \cdot 3MoO_3$). The β-phase is unstable in the temperature range 400–550°C, disproportionating on prolonged heating into α- and γ-molybdates. The region of stability of the β-molybdate is from 550–670°C.

INTRODUCTION

The successful application of bismuth molybdates to the catalytic oxidation of propylene or butene and to ammonoxidation of propylene, yielding, respectively, acrolein, butadiene, and acrylonitrile, has stimulated in recent years investigations on the physicochemical properties of Bi–Mo oxide catalysts and their correlation with catalytic activity and selectivity (*1–6*). Accordingly, interest has been revived in the chemical compounds existing in the Bi_2O_3–MoO_3 system (*7–12*). Out of the full range of the Bi/Mo compositions in this system, the range in which the atomic ratio Bi/Mo = 0.6–2.0 appears to be the most promising for catalytic applications, although there exist some discrepancies among various authors as to the exact value of this ratio for ensuring optimal catalytic parameters. The assignment of the optimum catalytic activity to a definite chemical compound is therefore an open problem. The range of compositions eligible for catalysis comprises three molybdates of the following formulae: $Bi_2O_3 \cdot MoO_3$, $Bi_2O_3 \cdot 2MoO_3$ and $Bi_2O_3 \cdot 3MoO_3$, called γ-, β- and α-phases, respectively, some of which, as shown recently (*9*) can occur in different modifications. The Russian workers (*5, 6*) relate the maximum activity to the presence of the β-phase, whilst Schuit and coworkers (*2*) claim that the γ-phase is the most active one, ascribing this activity to the presence of corner-sharing Mo–O octahedra, most distinct in the γ-phase. Evidence has also been reported indicating that amorphous catalysts in the Bi_2O_3–MoO_3 system are more active than crystalline phases (*13*). Out of the three molyb-

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dates written above, the existence of the β-phase was for some time disputed, the opinion having been that the catalyst with Bi/Mo = 1 was only a mixture of the two remaining molybdates. Further evidence indicated that this particular phase is formed by a solid state reaction occurring at temperatures higher than 550°C (*4*), or it could be formed at lower temperatures provided that the Bi/Mo ratio in the initial solutions is increased above unity (*14*). Any attempt at comparison of the results obtained by various workers and at formulating some general conclusions from the ample experimental material collected in various laboratories is hindered by the use of different methods of preparation of Bi–Mo–O catalysts. In view of this fact it seemed necessary, before any attempt to establish the correlation between the physicochemical and catalytic properties is undertaken, to determine the effect of the method of preparation and thermal treatment on the phase composition of the active phases. The present paper is concerned with catalysts of atomic ratio Bi/Mo = 1, corresponding to the composition of the β-phase, and is an attempt to determine the effect of the conditions of precipitation and of thermal treatment on the phase composition of the catalysts obtained.

EXPERIMENTAL

The preparations were obtained by mixing appropriate amounts of $Bi(NO_3)_3 \cdot 5H_2O$ in 1 *N* HNO_3 and ammonium paramolybdate (aqueous solution) at room temperature, a constant pH during the precipitation being maintained by adding simultaneously 5% aqueous ammonia. All reactants used were of Analar grade. The solutions were introduced dropwise and stirred vigorously during the whole course of the precipitation. The precipitates obtained were filtered or evaporated, dried at 120°C for 24 hr and annealed for various periods of time in the temperature range 300–700°C.

To study the effect of the conditions of precipitation on the structure of 1/1 catalysts, several series of preparations were obtained by precipitation at pH = 2 and pH = 7. The precipitates were allowed to stand in the mother liquor for various periods of time and were then separated from this liquor either by filtration or by evaporation. The pH of precipitation was selected bearing in mind the polymerization of molybdate ions in acidic media. In one series of preparations phosphorus, reported in the literature as one of the components of effective commercial Bi–Mo–O catalysts, was also added by introducing H_3PO_4 to the initial solution of paramolybdate, the ratio P:Mo being 1:12.

X-Ray analysis of the catalysts was performed with a Rigaku–Denki diffractometer, using CoK_α radiation. The identification of various molybdates present in the 1/1 samples prepared in different conditions was performed by comparing the X-ray diagrams of samples with the data given by Erman (*7, 8*) and Schuit (*4*), and with the diagrams of pure molybdates α and γ prepared by precipitation at the appropriate ratio Bi/Mo corresponding to the composition of these two compounds. The identification was confirmed by analysis of ir spectra.

The ir spectra of the solid samples in the nujol mull or in the form of discs pressed with KBr were recorded in the 400–1200 cm^{-1} region, using a Zeiss UR-20 spectrometer. The ir spectra of molybdates identified by X-ray analysis as α-, β- and γ-phases corresponded to those reported by Schuit *et al.* (*4*), Dewing (*15*) and Janik (*16*) for the respective compounds and like the latter data differed from the spectra reported by Trifiro *et al.* (*17*).

For some samples DTA and TGA analysis were also performed with the aid of a Paulik–Paulik–Erdey instrument, at rates of heating of 2.5, 5 and 12.5°/min.

The content of Bi and Mo in the catalysts was checked by chemical analysis. Molybdenum was determined colorimetrically in the form of Mo^V–EDTA complex, and bismuth by complexometric titration with EDTA.

RESULTS AND DISCUSSION

X-Ray analysis of precipitates dried at 120°C showed a rather poorly developed pattern, not sufficient for identification of particular molybdates, with the strongest line at d = 3.20. However, other characteristic lines of the β-phase were absent. To stimulate a higher degree of crystallization the precipitate was boiled in the mother liquor for several hours, but no improvement of the X-ray pattern was obtained. Accordingly, an attempt has been made to determine the structure of the precipitate by registering the ir spectra in the region 400–1200 cm^{-1}. The spectra of the dried Bi/Mo = 1/1 precipitates obtained at pH = 2 and pH = 7 in various conditions of subsequent treatment are shown in Fig. 1. For comparison the spectra of precipitates obtained at compositions corresponding to those of phase α (Bi/Mo = 2/3) and phase γ (Bi/Mo = 2/1) as well as spectra of crystalline molybdates α, β and γ are given in Fig. 2. As seen from Fig. 2 (curves I–III) the spectra of the precipitates are different for each of the Bi/Mo compositions, and although worse developed than the spectra of crystalline molybdates, they resemble these spectra in general features. On passing from com-

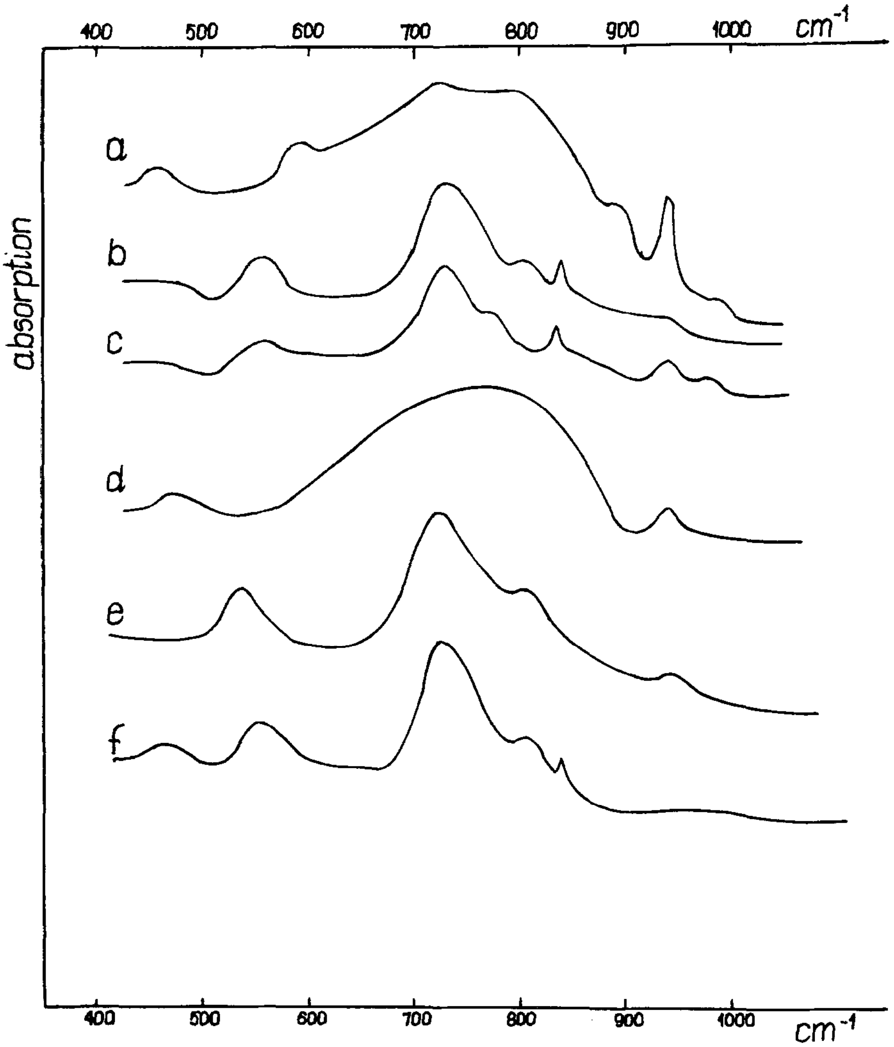

FIG. 1. Infrared spectra of the Bi/Mo = 1:1 precipitates: (a) samples precipitated at pH = 2; (b) precipitates obtained at pH = 7, filtered; (c) precipitates obtained at pH = 7, evaporated; (d) precipitate treated with 1% NH_3 for 48 hr; (e) precipitate treated with conc. NH_3 for 24 hr; (f) precipitate obtained at Bi/Mo = 2/1, pH = 7.

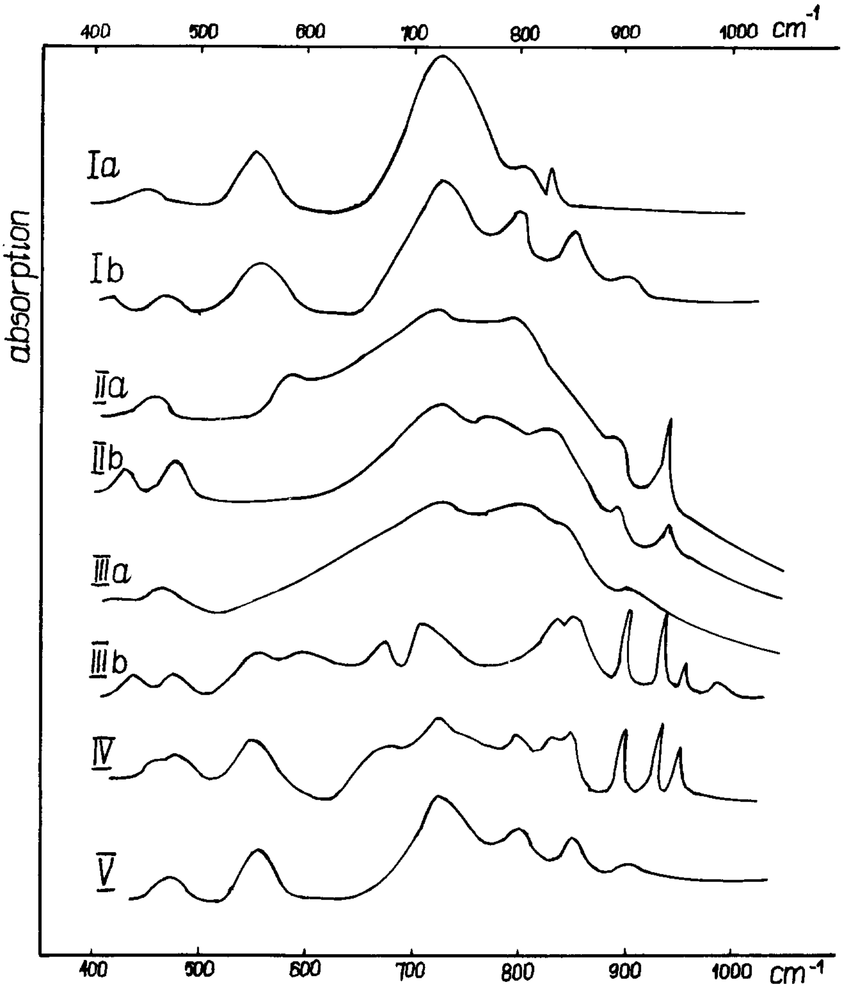

FIG. 2. Infrared spectra of precursors and of crystalline bismuth molybdates: I. Bi/Mo = 2/1, a-precipitate obtained at pH = 7, b-after calcination for 4 hr at 400°C (γ); II. Bi/Mo = 1/1, a-precipitate obtained at pH = 2, b-after calcination for 1.25 hr at 400°C (β); III. Bi/Mo = 2/3, a-precipitate obtained at pH = 2, b-after calcination 4 hr at 400°C (α); IV. Bi/Mo = 1/1, calcined 48 hr at 460°; V. Bi/Mo = 1, precipitated at pH = 7, calcined 4 hr at 400°C (γ).

position 2/1 to those richer in molybdenum one observes the broadening of the band with its center at 725 cm^{-1} and the appearance of bands between 900 and 1000 cm^{-1}, both in the case of crystalline molybdates and their precursors. The spectra of the Bi/Mo = 1/1 precipitates obtained at pH = 2 are similar, irrespective of the time of aging in the mother liquor, and show weak bands at 450 and 580 cm^{-1}, a very broad one with center at 725 cm^{-1} and shoulder at 800 cm^{-1}, a weak band at 895 cm^{-1} and a sharp one at 940 cm^{-1}. The spectra of the 1/1 precipitates obtained at pH = 7 are different, the bands at 580 cm^{-1} and 890 cm^{-1} and 940 cm^{-1} diminishing and bands at 550 and 840 cm^{-1} emerging in the spectrum.

The effect of the pH value in the course of precipitation on the structure of precipitates, supplemented by results of X-ray analysis described below, suggested that certain changes of the precipitate may take place in alkaline medium. To study it in more detail, the dried samples were treated with aqueous ammonia (concentrated and 1% solutions) for various periods of time, filtered, and the content of Mo in the

TABLE 1
KINETICS OF DISSOLVING OF MoO_3 FROM β-PHASE PRECURSOR IN AQUEOUS AMMONIA[a]

Time of treatment	Amount of Mo dissolved ($g\ MoO_3/g$ sample)	
	1% NH_3	conc. NH_3
0.5	—	0.094
1.0	—	0.130
2.0	—	0.150
4.0	—	0.165
12.0	0.069	0.174
24.0	0.079	0.165
48.0	0.093	0.178

[a] 1/1 preparation composed of $\gamma + MoO_3$ contains 0.177 g MoO_3.

filtrate and in the remaining precipitate was analyzed. Results of these determinations are shown in Table 1. As seen from this table the amount of Mo (expressed in g MoO_3/g of sample) removed by conc. NH_3 reaches a constant value after about 4 hr of treatment, the amount of Mo left in the precipitate corresponding exactly to the amount present in the γ-phase. The diluted ammonia is less effective in this respect. The ir spectra of precipitates treated with conc. NH_3 shown in Fig. 1*e* resemble closely the spectrum of the 1/1 precipitate obtained at pH = 7 (Fig. 1*b* and *c*) and the spectrum of the precursor of the γ-phase (Fig. 1*f*). They show an intense band at 725 cm^{-1}, a shoulder at 800 cm^{-1}, a sharp band at 835 cm^{-1} and broad bands around 460 and 550 cm^{-1}. The spectrum of the precipitate treated with diluted ammonia has features intermediate between those of the precipitate at pH = 2 and precipitate treated with conc. NH_3.

Since the X-ray patterns of precipitates did not permit us to identify the particular molybdates, the precipitates were annealed at higher temperatures to obtain crystalline molybdates. The behavior of preparations on heating was determined by registering the DTA and TGA curves. The DTA curves obtained for preparations precipitated at pH = 2 (Fig. 3a) and aged for various periods of time were similar, the heat effects being a weak endothermic effect at 520°C, followed by an endothermic peak at 675°C. Different DTA curves were registered in the case of precipitates obtained at pH = 7 as well as those obtained at pH = 2 and treated with conc. NH_3. The curves (Fig. 3b) show heat effects at 675, 915 and 950°C which can be related to the transition of the γ-phase to its high temperature form and melting of the material.

Already after short heating at 400°C a good diffraction pattern was obtained. The phase composition of 1/1 samples precipitated in various conditions and annealed

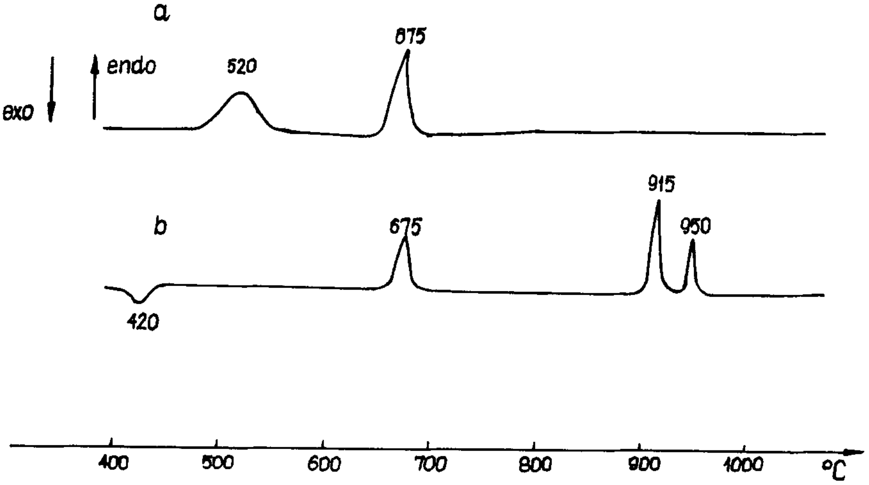

FIG. 3. DTA curves of the Bi/Mo = 1 catalysts: (a) sample obtained at pH = 2: (b) sample obtained at pH = 7, filtered.

TABLE 2

EFFECT OF CONDITIONS OF PREPARATION ON THE PHASE COMPOSITION OF 1/1 Bi–Mo CATALYSTS PREPARATIONS CALCINED AT 400°C

pH of precipitation	Manner of treating the precipitate	Bi/Mo = 1/1	Bi/Mo = 1/1 +P(Mo/P = 12)
2	filtered after: 2 hr	β	α,BiPO$_4$
	4 hr	β	
	12 hr	β	
	24 hr	β	
	evaporated after 2 hr	β	α,BiPO$_4$
	washed with H_2O till NO_3^- removed	$\beta(\alpha)$	
	washed with conc. NH_3 24 hr	γ	
	cryst. at 400°C + conc. NH_3 24 hr	β	
7	filtered after 2 hr	γ	
	evaporated after 2 hr	α,γ	α,BiPO$_4$

at 400°C for 1–6 hr is shown in Table 2. As indicated by the data summarized in this table, in samples precipitated at pH = 2 the β-phase is predominantly formed on annealing at 400°C, irrespective, of the time of aging of the precipitate and method of its separation from the mother liquor. When the sample was precipitated at pH = 7, only the formation of γ-phase was observed, due to partial dissolution of Mo at this pH. When this dissolution is prevented by evaporation instead of filtration, the mixture of γ and α molybdates is obtained. The γ-phase is formed also in the case when the precipitate obtained at pH = 2 is treated with ammonia and filtered. This observation together with the above mentioned ir and DTA data indicate that precipitation at pH = 7 is equivalent to washing of the dried precipitate, prepared at pH = 2, with conc. NH_3. It should be noted, however, that this definite part of Mo can be removed by NH_3 only from the dried precipitate; once the system crystallized to form the β-phase, no changes of the structure were observed by the action of this reagent. The stability of the crystallized samples towards the NH_3 treatment was confirmed by chemical analysis which showed only traces of Mo to be present in the filtrate, and by the ir data which showed that the β-phase remained unchanged after the treatment.

The results described so far seem to indicate that on precipitation of 1/1 Bi–Mo–O catalysts at different pH different precursors are formed which on heating crystallize into definite molybdates. The β-phase is most probably formed directly from its precursor obtained at pH = 2, without additional reactions in the solid state. The precursor of the β-phase transforms under the action of conc. NH_3 into the precursor of the γ-phase. The precipitation of the 1/1 preparations at pH = 7 gives preferentially the precursor of the γ-phase even when the loss of excess Mo (the case of evaporated samples) is prevented. The fact that even short annealing of the latter precipitates yields only a mixture of γ- and α-molybdates supports the hypothesis that the β-phase can be formed at lower temperatures only from its precursor obtained at pH = 2 and could be explained by fast reaction between the γ-phase and the excess of Mo yielding the α-phase. Such a reaction was in fact found to occur relatively easily even at lower temperatures (*18*).

The γ-phase (koechlinite) has a layer structure (*12*) composed of BiO-layers similar to those in BiOCl, and layers of [MoO_6] octahedra linked together through four corners. The remaining two corners of the octahedra link the MoO-layer with the BiO-layers so that all oxygen ions surrounding molybdenum cations are bridging oxygens. As the ir spectrum of the γ-phase is similar to that of its precursor we may conclude that the precipitate is also composed of [MoO_6] octahedra containing only bridging oxygens. As indicated by the similarity of ir spectra, the same structure appears as the result of removal by ammonia of one half of the molybdenum present in the precursor of the β-phase. The ir spectrum of the latter reveals the presence of a sharp band at 940 cm^{-1}, which is not present in koechlinite, but characterizes the spectrum of dimolybdates, composed of infinite chains of [MoO_6] octahedra sharing corners within the chain and with [MoO_4] tetrahedra bridging adjacent [MoO_6] groups (*19, 20*). Thus it seems plausible to assume that the precursor of the β-phase is built of layers of [MoO_6] octahedra and [MoO_4] tetrahedra, the latter being removed on action of ammonia, leaving layers of octahedra as precursor of the γ-phase. This is consistent with the suggestion mentioned by the Eindhoven school (*4*) as regards the structure of the β-phase.

In order to study the effect of thermal treatment on the stability of the β-phase and solid state reactions which may take place in the system, samples obtained at $pH = 2$ were annealed in the temperature range 400–700°C for various periods of time. Results of these experiments are summarized in Table 3. As seen from this table pure β-phase can be obtained at 400°C after a short period of annealing. At this temperature it is, however, unstable and decomposes into α- and γ-phases after longer periods of heating. This effect is more pronounced at 460°C. The presence of α- and γ-molybdates in 1/1 preparations annealed for longer times is also confirmed by ir spectra (Fig. 2, curve IV) which, besides bands characteristic of the β-phase, also show distinct bands of the γ-phase (at 550 cm^{-1}) and of the α-phase (902, 950 cm^{-1}). At 500–600°C even the prolonged annealing does not affect the phase composition, the β-phase being the only one registered in the X-ray diagrams. At about 700°C it decomposes again into the α-phase and the high temperature modification of the γ-phase (γ'), as generally recognized in the literature. It may be assumed that after the decomposition in the temperature range 400–500°C, β-phase may be again formed by the solid state reaction: $\alpha + \gamma = \beta$ occurring above 500°C. The peak at 520°C on the DTA curves could then be ascribed to this reaction. The region of stability of the β-phase would then correspond to the temperature range from about 520 to about 675°C where it decomposes into α and γ'. It should be noted that studies on the solid state reactions between various molybdate phases and pure MoO_3 and Bi_2O_3 (*18*) show that the reaction leading to formation of the β-phase commences at temperatures above 550°C. Similarly Schuit observed the formation of this phase at temperatures 560–620°C for preparations obtained by mixing precipitates of H_2MoO_4 and $BiO(OH) \cdot H_2O$. Hence precipitation appears to be the only method ensuring the preparation of the β-phase at lower temperatures, provided the appropriate value of pH is maintained on precipitation, and the calcination of the precipitate is carried out for not too long a time. The instability of this phase in the temperature region commonly used for conducting the catalytic reactions should however be borne in mind when searching for a correlation between the catalytic reactivity and phase composition of catalysts, and perhaps might account for differences in opinion among various workers as regards the most catalytically active molybdate.

TABLE 3

EFFECT OF TEMPERATURE AND TIME OF ANNEALING OF 1/1 Bi-Mo CATALYSTS ON THEIR PHASE COMPOSITION

Temperature (°C)	Time of annealing (hr)					
	1.25	6	11	16	24	48
400	β	β	β	$\beta(\alpha)$		$\beta(\alpha\gamma)$
460			$\beta\alpha\gamma$			$\beta\gamma\alpha$
500			$\beta\alpha\gamma$			
550			β		β	β
600			β		β	β
700			$\beta\alpha\gamma'$			

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