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The Catalytic Oxidation of Propylene

IV. Preparation and Characterization of α-Bismuth Molybdate

GEORGE W. KEULKS,* JEFFREY L. HALL,†
CHELLIAH DANIEL‡ AND KENICHI SUZUKI**

Department of Chemistry and Laboratory for Surface Studies,
University of Wisconsin—Milwaukee, Milwaukee, Wisconsin 53201

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A coprecipitation method is described which results in the preparation of the α-phase bismuth molybdate catalyst in high purity and which is reproducible. This preparation is based on the known principles of isopolymolybdate and molybdate heteropoly chemistry. The existence of a bismuth-molybdate heteropoly precursor having a stoichiometric ratio of bismuth to molybdenum of 2 to 3 is postulated using both the solution chemistry of the molybdates as well as X-ray diffraction measurements on several air-dried and oven-dried samples of precipitates obtained from the coprecipitation procedure.

INTRODUCTION

In recent years much work has been done in an attempt to correlate the catalytic activity for partial oxidation of hydrocarbons to the phase composition of various bismuth molybdate catalysts. Most of this work has been focused on the range of Bi/Mo composition of 0.6–2.0. Three principal phases have been identified in this range. They are the α-phase, the Erman or β-phase, and the γ-phase, having Bi/Mo ratios of 2/3, 1/1, and 2/1, respectively.

Some degree of controversy exists as to which phase exhibits maximum activity. Russian workers (*1*, *2*) maintain the β-phase exhibits maximum activity, while Batist, Lippens and Schuit, (*3*) suggest that γ-phase is the active phase.

In our studies we also have observed that catalytic activity and selectivity are critically dependent upon the method of preparation. Recent literature reports (*4*–*6*) clearly illustrate that this variation in catalytic behavior is no doubt due to the final composition of the catalytic mass and point to the importance of specifying exactly the conditions used to prepare the bismuth molybdate catalyst. Moreover, in an earlier paper of this series (paper II) (*7*), we reported that only the α-phase of bismuth molybdate underwent a reaction with iron to produce a catalyst which may be superior to bismuth molybdate.

It was our aim in this investigation to develop a coprecipitation method for the preparation of the α-phase of bismuth molybdate in high purity which could be easily reproduced by other workers in the area. We focused our attention on the α-phase because compared to the γ-phase less information is available concerning methods for its preparation in high purity and, consequently, if correlations are sought between catalytic activity and composition it is important to be able to characterize the catalytic activity of the pure phases. A detailed examination of catalytic be-

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* To whom correspondence should be addressed.

† Present address: Department of Chemistry, Montana State University, Bozeman, MT 59715.

‡ Present address: Catalysts and Chemicals India, Kerala, India.

** On leave from Ube Industries, Ltd., Central Research Laboratory, Ube-Shi, Yamaguchi Ken, Japan.

havior of the pure, α-, β-, and γ-phases is currently underway in our laboratory.

The coprecipitation method of preparation was selected for two reasons. First, it should be easily reproduced for it provides a method of obtaining a homogeneous mixture of the reactants that can be well characterized. Second, the solutions used to prepare the catalyst offer a substantial variety of pathways for studying the effects of other atoms such as iron or arsenic, i.e., the atom of interest can be added to the bismuth solution, the molybdenum solution, or the mixed solutions of bismuth and molybdenum, with the resulting effects on catalytic activity determined. Furthermore, catalysts having other structural properties, e.g., spinels and perovskites, can be prepared by a similar coprecipitation method (*8*). Thus, the effects of structural changes on catalytic activity also can be examined.

We have evaluated in some detail the coprecipitation method and the parameters affecting the precipitated catalyst by paying particular attention to the solution chemistry of the molybdate ion and its formation of isopoly anions as well as heteropoly compounds. The primary method of analysis of the samples of bismuth molybdate prepared by altering the various steps of the preparation was X-ray diffraction. From this study we have been able to develop a coprecipitation method which provides a means of obtaining a homogeneous mixture of a bismuth molybdate precipitate that can be easily duplicated provided the parameters affecting the preparation are rigorously followed.

EXPERIMENTAL METHODS

Reagents. Catalysts were prepared using Mallinckrodt AR grade ammonium paramolybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, and Fisher Certified bismuth nitrate, $Bi(NO_3)_3\cdot 5H_2O$. The masses of bismuth nitrate and ammonium molybdate used provided the desired mg-atoms of bismuth and molybdenum. A few catalysts were prepared using J. T. Baker CP bismuth subnitrate, $BiONO_3\cdot BiOOH$, rather than bismuth nitrate.

A solid state preparation was also attempted following a procedure outlined by Aykan (*9*). For this preparation Baker analyzed reagent grade molybdenum trioxide, MoO_3, and Mallinckrodt anhydrous bismuth oxide, Bi_2O_3, were used.

Preparations. The exact preparations of all of the catalysts examined in this study will not be given in order to conserve space, but will be provided upon request. The general preparation involves dissolving the bismuth nitrate in an acidic solution prepared by adding concentrated nitric acid (70% by volume) to pH 1.5. The bismuth nitrate solution is slowly added to the ammonium paramolybdate solution with constant stirring while maintaining a constant pH. A precipitate forms and is collected, dried for 2 hr at 115°C, and calcined for 20 hr at 450°C.

Parameters varied in this coprecipitation technique include the age of the acidified molybdate solutions, the pH of the acidified bismuth nitrate solution, the total concentration of the bismuth and molybdenum solutions, the aging of the bismuth molybdate precipitate, and the calcination procedure. The effects of these parameters on the catalyst preparation were examined both qualitatively and quantitatively by examining the X-ray powder patterns. Samples of the catalyst were taken during the preparations and usually included an air dried precursor, an oven dried (115°C) specimen, and the calcined sample. Sampling was varied as required.

X-Ray analysis. The X-ray powder patterns were obtained with a Jarrell-Ash diffractometer, using Cu $K\alpha$ radiation. Scans were made over a range from 10 to 60° at a scanning speed of 1°/min. The areas beneath the peaks were estimated using a grid pattern. A computer program designed for a Nova minicomputer was used to calculate the *d*-spacings as well as the relative intensities associated with each peak. Before analyzing a sample, the diffractometer was carefully aligned and optimized to give the most stable signal and highest signal-to-noise ratio. By this procedure, it was possible to determine the 2θ values with an accuracy of ±0.02°.

TABLE 1
CATALYST PREPARATION VARIABLES

	Atomic concn		Bismuth solution		Molybdenum solution		Precipitation back titration[d]	Age of precipitate	X-Ray data table
Sample[a]	Bi[b]	Mo[b]	Concn HNO_3[c] (ml)	Total vol. (ml)	Total vol. (ml)	Aged			
52	60	90	15	300	300	3 hr	No	144 hr	VII
66	60	90	15	300	300	10 min	No	27 hr	III
67	60	90	8	300	300	10 min	No	25 hr	III
68	60	90	15	300	300	10 min	Yes	20 hr	II
90	60	90	15	300	300	1 hr	Yes	20 hr	II
95	60	90	15	300	300	22 hr	Yes	20 hr	II, VII
97	60	90	15	300	300	1 hr	Yes	2 hr	V
101	6	9	15	300	300	1 hr	Yes	None	V, VII, VIII
104	6	9	15	300	300	1 hr	Yes	None	VIII
108	6	9	15	1200	200	1 hr	Yes	None	III, V, VI, VIII
110	6	9	15	1200	200	1 hr	Yes	None	VIII
112	12	18	15	2400	400	1 hr	No	20 hr	III, VI
116	60	90	60	1200	200	1 hr	Yes	None	VI
123	60	90	30	1200	200	1 hr	Yes	20 hr	III, V, VI

[a] All samples were calcined at 450°C for 20 hr except 101 and 112 which were calcined by a stepwise procedure.

[b] Mg-atom concentration.

[c] Total volume of concn HNO_3 used to dissolve the bismuth salt.

[d] Concn NH_4OH was added simultaneously during the precipitation to maintain a solution pH of 1.5.

RESULTS

We have summarized the catalyst preparation variables in Table 1 so that it can serve as a reference table for the discussion which follows.

Acidification of the molybdate solution. Earlier work performed in our laboratory as well as published data on the α-phase precipitate (*5*) indicated that the coprecipitation technique should be done at a low pH and room temperature. It was therefore necessary to lower the pH of the ammonium paramolybdate solution by adding concentrated nitric acid because the pH of the aqueous ammonium paramolybdate solution was usually between 5.1 and 5.4. Concentrated nitric acid was slowly added to the ammonium paramolybdate solution and a titration curve was obtained. Figure 1 shows typical plots obtained during this slow acid addition. The first curve is that for 90 mg-atoms of molybdenum in 300 cc of water, catalyst preparation 66; the second is for 9 mg-atoms of molybdenum in the same volume of water, catalyst preparation 101; and the third is for 9 mg-atoms of molybdenum in 200 cc of water, catalyst preparation 108. The molarities of these solutions, expressed in terms of molybdic acid, H_2MoO_4, become 0.3, 0.03, and 0.045 M, respectively. These titration curves are indicative of a well-buffered solution being formed as the pH is lowered. This topic is discussed more fully in the Discussion.

Age of the acidified molybdate solution. The equilibrium established between various condensed forms of the molybdate anion has been suggested to be attained both rapidly and slowly (*10–15*). Should the equilibrium be attained slowly, the importance of the aging time might be critical in the preparation of the catalyst. That is, whatever condensed form of the molybdate is present at a particular pH, the formation of this isopoly anion may be favored with time. Catalysts 68, 90, and 95 were prepared in identical fashions with the exception that the age of the acidified molybdate solution was varied. The acidi-

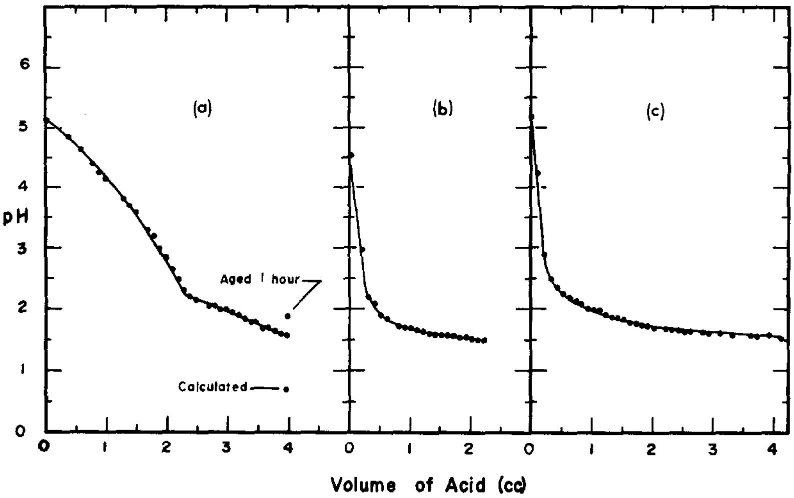

FIG. 1. Titration curves for the slow addition of concentrated nitric acid to the aqueous ammonium paramolybdate solution. (a) preparation 66; (b) preparation 101; (c) preparation 108.

fied bismuth nitrate solution was added to the ammonium paramolybdate solution 10 min after the ammonium paramolybdate solution was acidified for catalyst 68, 1 hr after acidification for catalyst 90, and 22 hr after acidification for catalyst 95. In the case of catalysts 90 and 95, the aging resulted in the formation of a white precipitate. The solution of acidified ammonium paramolybdate for catalyst 68 became turbid during the acidification but it was difficult to say whether the turbidity was due to a fine white precipitate or to a colloidal suspension being present. The X-ray data for the calcined catalysts obtained from these preparations is presented in Table 2.

The pH of the bismuth nitrate solution. The degree of condensation of the molybdate in the ammonium paramolybdate solution is a function of the acidity of that solution. The identity of the molybdate ion can range from the monomeric molybdate, MoO_4^{2-}, to the molybdenyl cation MoO_2^{2+} (*10*). Thus it is important to consider any pH changes of this solution during the preparation.

The bismuth nitrate solution is acidified with concentrated nitric acid in order to affect dissolution of this salt. The solubility of the bismuth nitrate is very limited in even relatively acidic solutions. Although reports in the literature (*5*) claim that 9 mg-atoms of the bismuth as the bismuth nitrate salt are soluble in 1200 cc of pH 1.5 aqueous solution, this claim was not reproducible in our laboratory. Several attempts at dissolving the appropriate quantity of bismuth nitrate in a pH 1.5 solution were unsuccessful. These attempts ranged from first dissolving the salt in 2.37 cc of concentrated nitric acid and then diluting with 1200 cc of water to preparing an acidified aqueous solution of pH 1.5 initially and then adding the salt to this solution.

The dissolution of the bismuth nitrate was accomplished using an aqueous solution of pH 1.3 or less. Because the pH of this bismuth solution does not match the pH of the acidified molybdate solution, during the addition of the bismuth solution to the acidified molybdate solution, the pH must necessarily change. The effect of this change in pH with respect to the identity of the molybdate existing in the solution was examined using both catalytic preparations as well as standard titration curves.

Catalysts 66 and 67 represent an examination of the effects of decreasing the volume of concentrated nitric acid used to dissolve the bismuth nitrate salt in 300 cc of water. In both instances 60 mg-atoms of bismuth were used, but the volume of concentrated nitric acid used was reduced from

TABLE 2
X-RAY DATA FOR AGED ACIDIFIED MOLYBDATE SOLUTIONS

Catalyst 68		Catalyst 90		Catalyst 95	
d (Å)	I/I_0 (%)	d (Å)	I/I_0 (%)	d (Å)	I/I_0 (%)
7.880	3	7.972	6	7.872	4
6.970	9	7.008	14	6.975	12
6.312	4	6.276	4	6.263	4
5.414	3	5.410	4	5.760	2
5.075	3	4.913	22	5.404	4
4.908	19	4.581	6	4.902	25
4.572	5	3.759	4	4.567	8
3.778	8	3.603	16	3.745	2
3.606	13	3.439	8	3.599	14
3.428	7	3.342	4	3.424	8
3.340	3	3.270	17	3.334	6
3.265	22	3.190	100	3.259	18
3.192	100	3.059	70	3.186	100
3.058	65	2.882	32	3.057	66
2.881	28	2.792	19	2.880	33
2.655	3	2.493	16	2.792	18
2.577	2	2.248	7	2.579	1
2.489	15	1.995	19	2.490	15
2.320	2	1.964	9	2.324	3
2.249	10	1.917	14	2.277	2
2.127	7	1.883	20	2.246	8
2.005	19	1.805	9	2.003	22
1.962	6	1.763	5	1.960	4
1.917	10	1.717	14	1.915	12
1.883	20	1.697	17	1.882	20
1.850	6			1.805	7
1.832	5			1.764	3
1.805	7			1.716	10

15 to 8 cc. The X-ray results are given in Table 3.

Several other catalysts were prepared using more dilute solutions of both the bismuth nitrate and the ammonium paramolybdate. These preparations involved dissolving 12 mg-atoms of bismuth in 2400 cc of water and 18 mg-atoms of molybdenum in 400 cc of water. As mentioned, even though the pH of the molybdenum solution was adjusted to 1.5, the pH of the bismuth solution could not be adjusted so as to match the 1.5 pH. Therefore, the pH of the bismuth solution was increased to only slightly greater than a pH of 1.0. The X-ray results for a representative sample (112) are presented in Table 3.

Other catalysts were prepared totally ignoring the acidity of the bismuth nitrate solution. These preparations involved the use of enough concentrated nitric acid so as to dissolve the bismuth nitrate in either 300 or 1200 cc of water, the number of mg-atoms of bismuth being either 6 or 60. The effect of this excess acid was nullified by back titrating with concentrated ammonium hydroxide during the mixing of the bismuth and molybdenum solutions. This procedure was adopted for most of the preparations. The X-ray data for two representative catalysts, 108 and 123, are given in Table 3.

We felt that the degree of polymerization of the isopolymolybdate anion in solution during the coprecipitation should be constant because should the polymer change during the coprecipitation procedure, the resultant product could conceivably be a mixture. To test the constancy of the isopolymolybdate's existence, four sets of solutions as outlined in Table 4 were prepared and mixed. The addition of the bismuth nitrate solution or the aqueous acid solution to the respective acidified ammonium paramolybdate solution was followed with a pH meter. The curves of pH versus volume of added solution, either bismuth nitrate or acid, are given in Fig. 2.

The total concentration of Bi and Mo. Important in this investigation is the total concentration of both bismuth and molybdenum expressed in both units of mg-atoms as well as molarity. Investigations by Trifiro, Hoser and Scarle (*5*) have shown that the coprecipitation technique requires that the bismuth and molybdenum atoms be present in a ratio of 2 to 3 in order to prepare the α-phase. Thus, this ratio was used in the preparations, but the molar concentration was varied considerably. The preparation of catalyst 123 involved dissolving the bismuth nitrate salt in 1200 cc of aqueous acid and the ammonium paramolybdate salt in 200 cc of water. Catalyst 101 and 108 duplicate the solution volumes of 97 and 123, respectively, but in this case, the number of mg-atoms of both bismuth and molybdenum are reduced to 6 and 9 mg-atoms, respectively. The X-ray results

TABLE 3
X-RAY DATA FOR EXAMINATION OF TOTAL ACIDITY

Catalyst 66		Catalyst 67		Catalyst 112		Catalyst 108		Catalyst 123	
d (Å)	I/I_0 (%)	d (Å)	I/I_0 (%)	d (Å)	I/I_0 (%)	d (Å)	I/I_0 (%)	d (Å)	I/I_0 (%)
7.915	2	7.887	2	7.001	2	7.965	1	6.289	2
6.454	10	6.992	11	6.34	3	6.992	6	4.905	10
5.407	4	4.908	19	5.09	3	6.267	3	4.569	2
5.104	4	4.567	8	4.90	7	4.910	11	3.606	15
4.892	19	3.786	15	3.750	2	4.579	4	3.422	4
4.576	11	3.611	17	3.603	11	3.797	8	3.334	5
3.787	16	3.449	10	3.425	8	3.599	11	3.263	23
3.600	16	3.338	8	3.330	5	3.448	5	3.184	100
3.439	14	3.264	30	3.262	22	3.351	4	3.122	2
3.334	6	3.194	100	3.186	100	3.264	29	3.054	89
3.263	39	3.059	66	3.053	78	3.192	100	2.879	34
3.187	100	2.882	29	2.879	31	3.059	75	2.788	23
3.057	82	2.790	17	2.789	19	2.881	26	2.657	4
2.878	33	2.666	11	2.657	47	2.792	18	2.493	21
2.791	19	2.492	17	2.509	5	2.660	5	2.297	6
2.657	11	2.321	4	2.479	10	2.493	16	2.247	13
2.504	8	2.252	10	2.347	3	2.318	3	2.122	4
2.481	8	2.122	7	2.334	3	2.285	5	2.096	3
2.325	2	2.005	19	2.322	7	2.249	5	2.003	34
2.247	12	1.962	7	2.282	3	2.126	3	1.963	15
2.122	5	1.918	14	2.247	11	2.092	1	1.939	4
2.003	21	1.883	19	2.123	7	2.004	20	1.916	30
1.963	8	1.845	9	2.004	26	1.961	4	1.884	28
1.916	16	1.806	10	1.960	10	1.918	11	1.843	9
1.881	24	1.718	10	1.937	2	1.883	19	1.805	13
		1.669	17	1.915	16	1.845	8	1.763	9
				1.882	29	1.803	5		
				1.848	7	1.718	11		

for this series of preparations are given in Table 5.

Age of the precipitate. A further consideration which appears to influence the quality of the recovered precipitate is the age of the precipitate after it has formed. The coprecipitation method presented in the literature (*5*) calls for immediate separation of the precipitate from the mother liquor. Catalyst 108 was prepared by dissolving 6 mg-atoms of bismuth in 1200 cc of aqueous nitric acid and 9 mg-atoms of molybdenum in 200 cc of water. Catalyst 112 was similar to 108 but the solution volumes as well as the number of mg-atoms were doubled. The precipitate that formed in the first preparation was separated immediately after forming while the latter preparation allowed the precipitate to stand overnight.

TABLE 4
SOLUTIONS USED TO OBTAIN FIG. 2 AND TEST THE CONSTANCY OF THE MOLYBDATE IN THE ACIDIFIED SOLUTIONS

Solution no.	9 mg-atom Mo diluted with (cc)	pH	6 mg-atoms Bi diluted with (cc)	pH	pH of 1200 cc of water
1	200	1.5	1200	1.2	—
2	200	1.5	—	—	1.5
3	200	1.0	—	—	1.0
4	200	1.5	1200	1.3	—

Another series of catalysts was prepared in which the number of mg-atoms of bismuth and molybdenum were increased to 60 and 90 mg-atoms, respectively. Again, the length of time before filtering the pre-

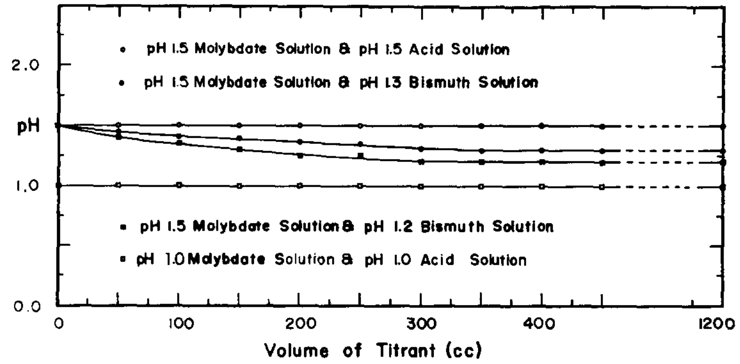

Fig. 2. Titration curves for the addition of either aqueous acid or a bismuth nitrate solution to the acidified ammonium paramolybdate solution.

TABLE 5

X-Ray Data for Preparations Examining Total Concentrations

Catalyst 97		Catalyst 123		Catalyst 101		Catalyst 108	
d (Å)	I/I_0 (%)	*d* (Å)	I/I_0 (%)	*d* (Å)	I/I_0 (%)	*d* (Å)	I/I_0 (%)
7.880	4	6.289	2	7.886	3	7.965	1
6.970	12	4.905	10	7.290	1	6.992	6
				6.964	12		
6.258	3	4.569	2	6.267	4	6.267	3
5.394	3	3.606	15	5.391	3	4.910	11
5.064	5	3.422	4	4.892	19	4.579	4
4.886	20	3.334	5	4.553	7	3.599	11
4.565	5	3.263	23	3.764	5	3.448	5
3.753	3	3.184	100	3.599	13	3.351	4
3.603	10	3.122	2	3.424	5	3.264	29
3.422	4	3.054	89	3.327	6	3.192	100
3.331	4	2.879	34	3.257	23	3.059	75
3.262	16	2.788	23	3.184	100	2.881	26
3.185	100	2.657	4	3.053	73	2.792	18
3.059	68	2.493	21	2.871	31	2.493	16
2.881	28	2.297	6	2.787	16	2.318	3
2.789	12	2.247	13	2.750	1	2.285	5
				2.504	6		
2.487	12	2.122	4	2.481	9	2.249	5
2.323	2	2.096	3	2.318	2	2.126	3
2.248	9	2.003	34	2.247	8	2.004	20
2.126	4	1.963	15	2.125	3	1.961	4
2.003	5	1.939	4	2.002	17	1.918	11
1.980	5	1.916	30	1.961	8	1.883	19
1.915	12	1.884	28	1.938	1	1.845	8
1.881	18	1.843	9	1.916	12	1.803	5
1.848	8	1.805	13			1.718	11
1.834	6	1.763	9				
1.803	6						

cipitate was varied. Catalyst 116 was filtered immediately after the bismuth solution had been added while catalyst 123 was prepared by allowing the precipitate to stand for 20 hr before separating it from the mother liquor. The X-ray data for these preparations is given in Table 6.

Calcination. The drying procedure and its effect on the catalyst preparation was examined. X-Ray patterns were obtained from several catalytic preparations or samples associated with each step in the drying procedure. The catalysts were dried by placing the filtered precipitate into a large porcelain dish and then allowing it to stand for 24–36 hr under ambient conditions or placing it into a static drying oven maintained at 115°C for 2 hr. Calcination was done in a muffle furnace. An air dried and oven dried sample of catalyst 52 was examined as well as a 15 and a 30 min sample of catalyst 95 as it was calcined at 450°C. Furthermore, X-ray patterns were obtained of two portions of catalyst 101 which were calcined following different heat treatment programs. The first portion, part A, was calcined using 1-hr heat treatments at temperature intervals at 100, 200, 300, 400 and 500°C. Part B of this catalyst was calcined at 450°C for 20 hr after being dried at 115°C for 2 hr. The X-ray results of this phase of the study are given in Table 7.

Bismuth subnitrate. Trifiro, Hoser and Scarle (*5*) suggested that the reaction forming the bismuth molybdate precipitate at the low pH used for mixing involved the bismuthyl cation, BiO^+. An attempt was

TABLE 6
X-RAY DATA FOR PREPARATIONS EXAMINING THE PRECIPITATE AGE

Catalyst 108		Catalyst 112		Catalyst 116		Catalyst 123	
d (Å)	I/I_0 (%)	*d* (Å)	I/I_0 (%)	*d* (Å)	I/I_0 (%)	*d* (Å)	I/I_0 (%)
7.965	1	7.001	2	7.873	4	6.289	2
6.992	6	6.34	3	6.959	12	4.905	10
6.267	3	5.09	3	6.254	4	4.569	2
4.910	11	4.90	7	5.391	4	3.606	15
4.579	4	3.750	2	4.881	18	3.422	4
3.599	11	3.603	11	4.548	5	3.334	5
3.448	5	3.425	8	3.746	1	3.263	23
3.351	4	3.330	5	3.655	2	3.184	100
3.264	29	3.262	22	3.597	11	3.122	2
3.192	100	3.186	100	3.448	2	3.054	89
3.059	75	3.053	78	3.330	8	2.879	34
2.881	26	2.879	31	3.262	18	2.788	23
2.792	18	2.789	19	3.184	100	2.657	4
2.493	16	2.657	47	3.127	1	2.493	21
2.318	3	2.509	5	3.058	71	2.297	6
2.285	5	2.479	10	2.879	29	2.247	13
2.249	5	2.347	3	2.784	19	2.122	4
2.126	3	2.334	3	2.505	5	2.096	3
2.004	20	2.322	7	2.481	11	2.003	34
1.961	4	2.282	3	2.324	5	1.963	15
1.918	11	2.247	11	2.247	7	1.939	4
1.883	19	2.123	7	2.123	2	1.916	30
1.845	8	2.004	26	2.091	1	1.884	28
1.803	5	1.960	10	2.001	18	1.843	9
1.718	11	1.937	2	1.963	5	1.805	13
		1.915	16			1.763	9
		1.882	29				
		1.848	7				

TABLE 7
X-Ray Data for Heat Treatments

Catalyst 52				Catalyst 95				Catalyst 101			
Air dried		Oven dried		15 min @ 450°C		30 min @ 450°C		Stepwise calc		One temp calc	
d (Å)	I/I_0 (%)	d (Å)	I/I_0 (%)	d (Å)	I/I_0 (%)	d (Å)	I/I_0 (%)	d (Å)	I/I_0 (%)	d (Å)	I/I_0 (%)
5.764	27	5.756	33			7.880	2	7.880	2	7.866	3
5.035	100	5.007	100	Amorphous		6.992	7	6.997	8	7.290	1
4.595	9	3.890	15			4.929	16	6.263	3	6.964	12
3.892	12	3.770	10			4.598	3	5.783	1	6.267	4
3.312	30	3.307	38			3.273	13	5.417	1	5.391	3
3.204	69	3.200	66			3.199	100	5.066	1	4.892	19
3.115	73	3.106	72			3.069	68	4.905	20	4.553	7
2.883	15	2.877	18			2.892	24	4.562	6	3.764	5
2.652	9	2.578	20			2.812	6	3.749	2	3.599	13
2.581	16					2.785	6	3.603	12	3.424	5
2.512	15					2.663	2	3.427	6	3.327	6
2.306	8					2.572	9	3.330	6	3.257	23
2.111	12					2.259	2	3.269	18	3.184	100
1.983	18					2.094	1	3.191	100	3.053	73
1.927	13					2.066	1	3.056	73	2.877	31
1.850	13					2.005	16	2.881	29	2.787	16
1.801	8					1.919	5	2.793	18	2.750	1
1.706	7					1.886	13	2.758	1	2.627	1
1.689	7							2.660	1	2.504	6
1.640	7							2.512	3	2.481	9
								2.485	10	2.343	1
								2.323	3	2.318	2
								2.278	4	2.247	8
								2.248	8	2.125	3
								2.183	1	2.002	17
								2.126	5	1.961	8
								2.094	1	1.938	1
								2.005	19	1.916	12

made in this study to try to favor the formation of this cation in solution by using the bismuth subnitrate salt, $BiONO_3 \cdot BiOOH$. In preparations 104 and 110, 6 and 9 mg-atoms of Bi and Mo, respectively, were used but the total concentrations were varied: 300 cc of the aqueous solutions were used to dissolve both salts in preparation 104 while 1200 cc of aqueous nitric acid were used to dissolve the bismuth subnitrate and 200 cc of water were used to dissolve the ammonium paramolybdate in preparation 110. These preparations compare in concentrations to those numbered 101 and 108. The difference in both sets of the preparations is the source of the bismuth ions, namely the latter two preparations used the bismuth nitrate salt $Bi(NO_3)_3 \cdot 5H_2O$ while the former two preparations used the bismuth subnitrate. The X-ray data for the four catalysts is given in Table 8.

Discussion

Isopoly anion identity. The coprecipitation method for preparing the pure α-phase bismuth molybdate catalyst involves several distinctive steps. These steps include the slow acidification of the ammonium paramolybdate solution, addition of the bismuth nitrate solution to the acidified ammonium paramolybdate solution with subsequent precipitate formation, filtration,

TABLE 8
X-RAY DATA FOR COMPARING TWO SOURCES OF BISMUTH IONS

Catalyst 101-B $Bi(NO_3)_3 \cdot 5H_2O$		Catalyst 104 $BiONO_3 \cdot BiOOH$		Catalyst 108 $Bi(NO_3)_3 \cdot 5H_2O$		Catalyst 110 $BiONO_3 \cdot BiOOH$	
d (Å)	I/I_0 (%)	d (Å)	I/I_0 (%)	d (Å)	I/I_0 (%)	d (Å)	I/I_0 (%)
7.866	3	8.140	2	7.965	1	6.964	8
7.290	1	7.873	3	6.992	6	6.312	3
6.964	12	6.948	7	6.267	3	5.407	1
6.267	4	6.258	3	4.910	11	5.075	3
5.391	3	5.957	3	4.579	4	4.902	15
4.892	19	5.745	1	3.797	8	4.579	5
4.553	7	5.404	2	3.599	11	3.739	1
3.764	5	5.058	1	3.448	5	3.603	15
3.599	13	4.897	17	3.351	4	3.423	7
3.424	5	4.772	1	3.264	29	3.332	4
3.327	6	4.558	5	3.192	100	3.263	17
3.257	23	3.748	3	3.059	75	3.184	100
3.184	100	3.600	10	2.881	26	3.057	79
3.053	73	3.419	3	2.792	18	2.880	33
2.877	31	3.310	6	2.660	5	2.789	16
2.787	16	3.255	22	2.493	16	2.657	4
2.750	1	3.184	100	2.318	3	2.499	9
2.627	1	3.057	54	2.285	5	2.475	5
2.504	6	2.881	24	2.249	5	2.345	1
2.481	9	2.789	20	2.126	3	2.323	3
2.343	1	2.731	2	2.092	1	2.285	3
2.318	2	2.695	3	2.004	20	2.246	8
2.247	8	2.576	1	1.961	4	2.181	1
2.125	3	2.489	8	1.918	11	2.125	5
2.002	17	2.313	1	1.883	19	2.003	19
1.961	8	2.282	2	1.845	8	1.959	7
1.938	1	2.245	6	1.803	5	1.911	5
1.916	12	2.180	1	1.718	11		

drying, and finally calcination. Each of these steps has been examined experimentally and optimized in order to develop a preparation that is both reproducible and gives a α-phase catalyst which appears pure by X-ray diffraction. The object of this discussion is to integrate the empirically defined steps with a knowledge of the postulated chemistry involved in each step.

The molybdate anion can polymerize to form a variety of isopoly derivatives in solution. The extent of the polymerization is dependent upon the concentration of the molybdate, the pH, the age of the solution, and the temperature of the solution. At very low concentrations of molybdate, less than 0.0003 *M*, Carpeni (*16*) has shown that only the normal molybdate anion, MoO_4^{2-}, exists throughout the entire pH range. However, at higher concentrations of molybdate, the normal molybdate anion is only stable above a pH of 6.5. As the acidity of the solution is increased, the normal molybdate anions can condense to form higher polymers (isopoly anions) until the isoelectric point is reached and molybdic acid precipitates. Further acidification causes the precipitate to dissociate and to form molybdenyl cations, MoO_2^{2+}.

At room temperature, decreasing the pH below 6.5 leads to the formation of the heptamolybdate anion, $Mo_7O_{24}^{6-}$, by the following reaction:

$$7MoO_4^{2-} + 8H^+ \rightleftarrows Mo_7O_{24}^{6-} + 4H_2O.$$

This reaction is practically complete at pH of 4.5. At higher acidities this heptamer becomes protonated to a maximum of a diprotonated anion as described by the equations,

$$Mo_7O_{24}^{6-} + H^+ \rightleftarrows HMo_7O_{24}^{5-},$$
$$HMo_7O_{24}^{5-} + H^+ \rightleftarrows H_2Mo_7O_{24}^{4-}.$$

Further acidification, between a pH of 2.9 and 1.1, the octamolybdate simultaneously forms and can become protonated according to the following equilibria:

$$8H_2Mo_7O_{24}^{4-} + 4H^+ \rightleftarrows 7Mo_8O_{26}^{4-} + 10H_2O,$$
$$Mo_8O_{26}^{4-} + H^+ \rightleftarrows HMo_8O_{26}^{3-},$$
$$HMo_8O_{26}^{3-} + H^+ \rightleftarrows H_2Mo_8O_{26}^{2-},$$
$$H_2Mo_8O_{26}^{2-} + H^+ \rightleftarrows H_3Mo_8O_{26}^{-}.$$

The formation of higher aggregates is possible if the hydrogen ion to normal molybdate anion ratio is greater than 1.5. At a pH of 0.9 the isoelectric point of molybdic acid is reached and molybdic acid precipitates. At lower pH values, the precipitate redissolves and forms cationic species, using the octamolybdic acid to illustrate

$$H_3Mo_8O_{26}^{-} + 17H^+ \rightleftarrows 8MoO_2^{2+} + 10H_2O.$$

Throughout this process, no dimers or trimers of the molybdate exist in solutions held at room temperature (*10*).

The first step of the coprecipitation method is to prepare a molybdate solution by dissolving the ammonium paramolybdate salt in water which, on dissolving, is slowly acidified with nitric acid to a pH of 1.5. Figure 1 illustrates three different acidification curves for various concentrations of the ammonium paramolybdate used in the catalytic preparations. Several features of these curves can be explained using the chemistry of the isopolymolybdates.

Initially, the pH of the ammonium paramolybdate solution is between 5.1 and 5.4. Only in the case of the most dilute solution is the initial pH lower. This initial pH is within the paramolybdate's range of existence. Thus, the ammonium paramolybdate used to prepare the solution appears to maintain the identity of the anion of the salt. The ammonium paramolybdate solution is then slowly acidified to the pH of 1.5 which, as briefly described above, must involve the condensation of the heptamer to a higher polymer. The identity of this higher aggregate has been assumed to be an octamer. The first curve in Fig. 1 is that obtained when acidifying a 0.3 *M* solution of the ammonium paramolybdate. This is the most concentrated solution examined, and the appearance of a break in the acidification curve is indicative of a system that is being well buffered. Therefore, both protonation of the heptamer and condensation to the octamer are felt to occur and thus give the solution an exceedingly great buffering capacity. The suggested equilibria describing this buffered system are:

$$Mo_7O_{24}^{6-} + H^+ \rightleftarrows HMo_7O_{24}^{5-},$$
$$HMo_7O_{24}^{5-} + H^+ \rightleftarrows H_2Mo_7O_{24}^{4-},$$
$$8H_2Mo_7O_{24}^{4-} + 4H^+ \rightleftarrows 7Mo_8O_{26}^{4-} + 10H_2O,$$
$$Mo_8O_{26}^{4-} + H^+ \rightleftarrows HMo_8O_{26}^{3-},$$
$$HMo_8O_{26}^{3-} + H^+ \rightleftarrows H_2Mo_8O_{26}^{2-}.$$

The break in the first titration curve occurs at a pH of 2.3 and is felt to be the result of the condensation step forming the octamer. The initial portion of the first acidification plot is most readily associated with the protonation steps of the heptamer. Because the solution being examined is quite concentrated, the local concentration of the heptamer is very high and the concentrated nitric acid which is used during the acidification is readily consumed by the heptamer thus forming the protonated species. The effect is to give a curved shape to the initial portion of the acidification plot. This argument anticipates that the solutions of lesser concentrations would result in a more rapid decrease of the pH of the initial portion of the acidification curve because the local concentration of the heptamer in the vicinity of the added acid would be less than that for a more concentrated solution. The curves for sample 101 and 108 show sharper decreases for solutions of concentrations of 0.03 and 0.045 *M* in molybdic acid, respectively.

A critical question concerns the identity of the polymer existing in these less concentrated solutions. Again, referring to Fig. 1, the pH breaks, i.e., the portion of the curve where the slope changes and which is assumed to be the point where condensation to the octamer begins, is at pH 2.2 for curve 101 and 2.4 for curve 108. These pH values are very closely associated with the pH 2.3 for curve 66, the most concentrated solution. Because these breaks appear at nearly the same pH, the identity of the isopolymolybdate is felt to be the same, viz, the octamolybdate. This assumption is further supported by the pH range assumed to be associated with the octamer's existence. Moreover, these experiments offer strong evidence that this isopoly anion is present in all of the initially acidified ammonium paramolybdate solutions.

Acidification of the bismuth nitrate solution. The preparations examined in this study used basically two methods for adding the acidified bismuth nitrate solution to the acidified ammonium paramolybdate solution. In one case, enough concentrated nitric acid was added to dissolve the bismuth salt regardless of the solution's final pH. Thus, when adding this acidified bismuth nitrate solution to the acidified ammonium paramolybdate solution, the mixture was maintained at a constant pH of 1.5 with simultaneous addition of concentrated aqueous ammonia. The other method was only used for the most dilute bismuth nitrate solutions, being an attempt at duplicating Trifiro, Hoser and Scarle's (*5*) method of preparation. In this case, the pH of the bismuth nitrate solution was closely matched to the pH of the acidified ammonium paramolybdate solution.

In the first method, the identity of the isopolyanion is assumed to remain unchanged for neither the pH nor the total number of hydrogen ions present are changed. This latter parameter is also important because an increase in the total number of hydrogen ions present without subsequent increase in the total number of molybdates present can result in further condensation or even decomposition reactions thus changing the identity of the isopolyanion in the mixed solutions. Trifiro's method of pH matching with subsequent addition of the acidified bismuth nitrate solution to the acidified ammonium paramolybdate solution increases the total number of hydrogen ions in the solution and is thus subject to this latter parameter. What effect this may have on the isopolyanion identity was examined using a pH meter. This method of examination assumes that any reaction, i.e., condensation or decomposition, would result in an observable titration curve break as was observed during the initial acidification of the ammonium paramolybdate solution. Table 4 and Fig. 2 illustrate the results. Referring to Fig. 2, addition of the aqueous solutions of pH 1.5 and 1.0 prepared by mixing appropriate amounts of concentrated nitric acid with 1200 cc of water to the solutions of the ammonium paramolybdate acidified to pH 1.5 and 1.0 show no observable change throughout the range of addition. Thus the identity of the isopolyanion remains unchanged during the dilution of the acidified ammonium paramolybdate solution and concomitant increase in the total number of hydrogen ions in that solution. The remaining two curves of Fig. 2 represent the addition of the bismuth nitrate solution. The pH values of these bismuth solutions were 1.3 and 1.2. These pH values are slightly less than 1.5. Although the plots for the addition of these solutions to the acidified ammonium paramolybdate solutions show a slight decrease in the pH during this addition, this decrease is attributed to the initial difference in the pH of both solutions used to obtain the bismuth nitrate–ammonium paramolybdate mixture. The decrease in pH halts after the pH of the mixture has matched the initial pH of the acidified bismuth nitrate solution. Therefore, the isopolyanion that initially exists in the acidified ammonium paramolybdate solution remains constant throughout the preparation outlined by Trifiro.

A series of catalysts was made in order to examine the effect of the acidity of the bismuth nitrate solutions on the purity of the calcined product obtained as determined by X-ray analysis. Preparations 66 and 67 varied the acidity of a rather concentrated solution of bismuth nitrate (60 mg-atoms of bismuth/300 cc of water) while preparation 112 used a more dilute solution of the bismuth nitrate (12 mg-atoms of bismuth/2400 cc of water) and a higher pH. Still another series of catalysts, 123 and 108 being representative samples, were prepared in which the acidity of the bismuth nitrate solutions was not controlled. That is, enough acid was added to the bismuth nitrate salt in order to effect dissolution regardless of the resultant pH. However, on adding these solutions to the acidified ammonium paramolybdate solution, the pH was maintained constant by back titrating with concentrated aqueous ammonia. For preparations 66 and 67 the acidified bismuth nitrate solution was slowly added to the acidified ammonium paramolybdate solution. Preparation 112 attempted to match the pH values of both solutions prior to mixing them. The X-ray results for this series of catalysts are given in Table 3.

The data in Table 3 can be compared with the most characteristic lines for the α-phase and the γ-phase taken from the work of Erman *et al.* (*21*), Batist *et al.* (*22*), and Aykan (*9*). Catalyst 66 does not appear to be very pure for it has several unidentified lines at $d = 6.45, 5.98, 5.10, 2.58, 2.50$ (Å). The filtrate from the separation of the coprecipitated product and mother liquor was evaporated and the residue was calcined. The X-ray analysis of this sample was observed to contain predominately γ-phase bismuth molybdate as well as several unidentified lines. Table 9 summarizes the X-ray results for the filtrate.

TABLE 9
X-RAY DATA FOR RESIDUE IN FILTRATE OF PREPARATION 66

d (Å)	I/I_0 (%)
8.155	8
3.767	1
3.255 3.216	31
3.156	100
2.823	7
2.746	34
2.699	23
2.604	2
2.490	8
2.276	2
1.992	5
1.941	14
1.919	28
1.654	29
1.632	20
1.576	11

It appears that the contaminant in the catalyst which was to be pure 2/3 is perhaps molybdenum trioxide. Lines characteristic of MoO_3 are found in both 66 and 67. In both of these preparations, the measured pH of the bismuth nitrate solution was less than 1. Preparation 66 used 15 cc of concentrated nitric acid to dissolve the bismuth nitrate salt while preparation 67 used 8 cc of the acid. Thus the initial pH of the bismuth nitrate solution was less than 1 and, after adding this solution to the acidified ammonium paramolybdate solution, the final pH of the mixture was less than 1. The pH drop experienced by the molybdate isopolyanion in one case was 0.8 pH units while in the other case was 0.7 pH units. By reducing this final pH to something less than 1, it appears that the molybdate polymer is changing in the solution. Although the direction of this change, i.e., further condensation or decomposition of the polymer, is not well established, the fact that the pH has passed the isoelectric point of molybdic acid and is now in the pH range for the formation of the molybdenyl cation does appear to have impact on the purity of the catalyst. Furthermore, it should be noted that the pH was measured with a pH meter using a glass electrode vs saturated calomel electrode system. Thus the final measured pH is within the range of the acid error for a glass electrode. It is reasonable to assume that the pH may indeed be even lower than that recorded by the pH meter.

Catalyst 112 was indeed very pure α-phase bismuth molybdate. This preparation follows Trifiro's basic method (*5*) of coprecipitation but simply doubles both the mg-atoms of bismuth and molybdenum and the total solution volumes. The pH of the two solutions were closely matched to pH 1.5. It has been demonstrated above that the molybdate polymer does not change during the addition of the bismuth nitrate solution to the acidified ammonium paramolybdate solution. Thus the isopolyanion remains constant throughout the addition and the catalyst obtained is quite pure.

Finally, the last method of preparation investigated in this series, namely preparations represented by catalysts 108 and 123, are typical of the majority of the preparations. In both instances Trifiro's volumes, namely 200 and 1200 cc of solution for the ammonium paramolybdate and the bismuth nitrate, respectively, were used to dissolve the salts. Catalyst 108 also used Trifiro's mg-atom ratio of 6:9 bismuth to molybdenum while 123 used more concentrated solutions, namely 60:90 mg-atoms of bismuth to molybdenum. In these preparations the bismuth nitrate solution was acidified with sufficient acid to dissolve the salt but back titrated with concentrated aqueous ammonia during the mixing of the bismuth nitrate solution with the acidified ammonium paramolybdate solution. The precipitate that was formed was filtered at different times, i.e., 108 was filtered immediately while 123 was allowed to stand for 20 hr before separating. The effect of aging is discussed below but appears to be a simple analytical problem. This method of addition, using 123 as the example, gives a catalyst of excellent purity. Catalyst 108 seems to have some molybdenum trioxide as a contaminant ($d = 3.79$ and $2.66\,\text{Å}$). Catalyst 123 shows no detectable impurities by X-ray analysis and again, using the relative intensity for $d = 3.05\,\text{Å}$, the catalyst compares quite well with that given by Aykan (*9*), namely 89% compared with 90%. Thus the two methods of preparation which give catalysts of high purity are preparation 112 and preparation 123. Preparation 112 is limited in that the bismuth nitrate is very poorly soluble in all but the most acidic media. Thus the number of mg-atoms used in this preparation is indeed an upper limit, for more concentrated solutions result in either a bismuth hydroxide precipitate forming or a bismuthyl salt precipitating, both being very insoluble. Preparation 123 on the other hand, also gives a good α-phase catalyst but uses more concentrated solutions with subsequent back titrating to maintain a constant pH. In each case, the isopolyanion present is held constant. It is this fact that suggests that both of these methods give good α-phase catalysts while the first method, with the wide ranging pH values and subsequent changes in the molybdate aggregate existing in solution gives poorer products, i.e., they are less crystalline and are contaminated with impurities.

Aging the acidified ammonium paramolybdate solution. The above discussion has suggested that the isopolymolybdate anion is the octamer. This polymerized anion maintains its integrity in all of the initially acidified molybdate solutions as well as all the most dilute mixtures of the ammonium paramolybdate–bismuth nitrate used in this study. The isopolyanion that forms in the acidified molybdate solution, be it the octamolybdate or some other aggregate, must be present throughout the preparation in order to obtain the least perturbed preparation for the α-phase. Figure 2 attempted to establish this constancy. Thus it is imperative that all the parameters which support the existence of the isopolymolybdate be optimized.

Several authors examining the equilibration process for the formation of the isopolymolybdates have reported that the attainment of the equilibrium proceeds quite slowly (*10–13*). Another group of authors examining the heteropoly formation of the molybdophosphoric acid (*14*) have also found that the age of the molybdate solution influenced the preparation. The initial claim of a slow equilibration was qualitatively in agreement with some of our own observations. The acidification of the ammonium paramolybdate solution could be done by either slowly adding the concentrated nitric acid or rapidly adding it. The results shown in Fig. 1 were obtained using slow drop by drop addition of the acid. When the acid was rapidly added, the pH dropped to 1.5 very rapidly without giving any indication of establishing a well-buffered system. The volume of acid used was also less for the latter method of addition. Thus it would seem that the equilibria are slowly attained. Further support of this conclusion can be obtained from Fig. 1. The first plot of the acidification of the molybdate solution shows an increase in the pH after 1 hr of aging. That is, the pH had been reduced to a pH of 1.55 but, after 1 hr, had increased to a pH of 1.90. This increase was not categorically observed for each sample of the ammonium paramolybdate used to prepare the catalysts. However, its appearance in the most concentrated solution is indicative of an equilibrium that is attained quite slowly. Other acidification curves that were obtained for more dilute solutions also supported this slow equilibration concept for, during the addition of the concentrated nitric acid, the pH was initially quite low when the acid first entered the solution but after several moments, the pH would begin to increase indicating that the hydrogen ions were slowly being consumed. During this acid addition, the solution was vigorously stirred with an electric stirrer.

Several catalysts were prepared in which the age of the acidified ammonium paramolybdate solution was varied. Catalyst preparations 68, 90, and 95 investigated the effect of aging. The X-ray results for this series of catalysts are given in Table 2. In comparing the lines for the catalysts listed in Table 2 with those lines given in the literature, we found that several of the lines are missing in all three preparations. For instance, $d = 2.79$ Å is not present in catalyst 68 nor is $d = 2.51$ Å present in any of the preparations. However, comparing the overall agreement between the d-spacing experimentally obtained with those listed in the literature, the agreement is seen to be quite satisfactory. Lines associated with the other phases of bismuth molybdate catalysts as well as those lines normally associated with bismuth oxide and molybdenum trioxide are not present. Of the three preparations, the 90 preparation which was aged for 1 hr appears to be the best when comparing the relative intensity of $d = 3.058$ Å with that of Aykan's solid state preparation (*9*), i.e., 90% for Aykan and 70% for 90.

Heteropoly precursor. The identity of the α-phase precursor as obtained from the coprecipitation technique has not been unequivocally established. Several points about the precursor can be inferred from the experimental investigations reported herein. First and perhaps foremost, the precursor must form in a ratio of bismuth to molybdenum that duplicates the ratio of the α-phase bismuth molybdate, namely 2 to 3. Several of the preparations evaporated the filtrate to dryness after collecting the precipitate and found material to be present after calcining the residue. Thus some molybdenum and some bismuth must remain in solution. However, the catalysts prepared, particularly 112 and 123, give very good α-phase samples. Therefore, the stoichiometry of the precipitate must mirror the 2/3 ratio of the catalyst. Should it not, the precipitate would contain excess bismuth oxide or molybdenum trioxide after calcination. Were this excess to be within the experimental limits of detectability for the X-ray analysis, the catalyst would show characteristic lines for either of these oxides. Aykan (*9*) has demonstrated that a mixture of the oxides of bismuth and molybdenum in a ratio of 2 to 3 bismuth to molybdenum atoms can react in the solid state during calcination to form the α-phase sample. However, the likelihood of precipitating an excess of bismuth and molybdenum in such a stoichiometric ratio does not seem plausible.

The arguments presented for identifying the isopolyanion in the acidified ammonium molybdate solution suggest that the octamer is the molybdate aggregate that is present. More important than the actual identity of the isopolymolybdate is its constancy of existence. The octamolybdate anion is represented as $Mo_8O_{26}^{4-}$. The isopolyanion has been shown to exist throughout the range of the bismuth nitrate addition for those solutions that are prepared using Trifiro's method (Fig. 2) and postulated as existing in the more concentrated solutions because the pH was held constant during the mixing. However, if the octamolybdate anion were incorporated into the precursor, the 2/3 ratio of bismuth to molybdenum would be very difficult to obtain. However, the presence of this polymer or rather the constancy of existence for a polymer appears to be quite necessary. Catalyst preparations in which the pH varies greatly during the addition and thus possibly the molybdate isopolyanion in solution give less pure samples (66 and 67).

The acidification of the molybdate solution is accompanied in the more concentrated cases with precipitate formation. The precipitate is milky white but X-ray analysis of a collected sample of this precipitate shows that the precipitate is amorphous both after air drying and after oven drying. The precipitate may be some form of the octamolybdate incorporating both hydrogen ions and ammonium ions as charge balancing cations in this amorphous phase. Again, the exact identity of this molybdate precipitate is unknown. However, during the addition of the bismuth nitrate solution to this acidified ammonium paramolybdate solution, this white amorphous phase was observed visually to change in color becoming pale yellow to pale green. The exact color is difficult to establish and only qualitative at best, yet it does point to some type of modification of this precipitate accompanied with the addition of the bismuth nitrate, for simply adding an aqueous acid solution of the same pH and volume as the bismuth nitrate solution does not seem to change the color of the precipitate.

Further evidence regarding the possible precursor can be inferred from the catalyst preparations using the bismuth subnitrate, 104 and 110. These preparations are identical to those numbered 101 and 108, varying only in the source of the bismuth. The latter two preparations, using bismuth nitrate salt, would probably precipitate the bismuth ion as the hydroxide, $Bi(OH)_3$, on addition of the bismuth nitrate solution to an acidified ammonium paramolybdate solution at pH 1.5. The former two preparations obtain the bismuth from a salt that contains the bismuthyl ion, BiO^+, which would then be precipitated on adding to the acidified molybdate solution. Table 8 compares the X-ray results for these four preparations. Those preparations using the bismuth subnitrate have lines that correspond to impurities. For instance, catalyst 104 is contaminated with γ-phase bismuth molybdate as well as a slight amount of molybdenum trioxide ($d = 2.31$ Å). Preparation 110, although apparently free from γ-phase bismuth molybdate and either bismuth oxides or molybdenum oxides, has two unidentified lines at $d = 3.74$ and 2.50 Å. Preparation 108, the counterpart of 110, is contaminated with molybdenum trioxide while the counterpart of 104, i.e., 101 seems to be contaminated with a small amount of γ-phase. The X-ray data do not seem to provide any quantitative information on which to base a conclusion as to the superiority of one salt versus the other, and thus the possible identity of the heteroatom. On a qualitative basis, however, the diffractometer patterns for those catalysts using the bismuth nitrate salt indicate that these catalysts exhibit better crystallinity. The peaks are very sharp and more defined than for similar peaks for those preparations using the bismuth subnitrate salt. This qualitative observance seems to indicate that the bismuth ion associated with the precursor is not the bismuthyl ion.

X-ray data of the air dried and oven dried bismuth molybdate precipitate is displayed in Table 7. Of particular interest for these two samples is the major peak, that is the d-spacing associated with 100% relative intensity. Although the d-spacing has shifted slightly after a mild heat treatment in a drying oven for 2 hr ($d = 5.035$ Å to $d = 5.007$ Å), this line is not a characteristic line for any of the bismuth molybdate phases, the bismuth oxide, molybdenum trioxide, ammonium paramolybdate, nor calcined ammonium paramolybdate. Also, none of the characteristic α-phase lines are present. As mentioned, the initial precipitate formed when acidifying the more concentrated solutions of the ammonium paramolybdate is, by X-ray analysis, amorphous. This amorphous compound, after adding the bismuth nitrate solution, gives an X-ray pattern that does not match any of the known patterns for various compounds associated with bismuth and molybdenum, nor does it contain peaks associated with the α-phase. Furthermore, samples of a catalyst preparation removed from the muffle furnace 15 min into the heat treatment showed the sample to be totally amorphous yet another sample removed 15 min later showed the characteristic α-phase lines. We feel that this is indicative of a heteropoly compound formed between bismuth and the molybdate, the stoichiometery of which duplicates the ratio of bismuth to molybdenum in the α-phase modification. This heteropoly forms an amorphous phase during the heat treatment. From this amorphous phase which contains the bismuth and molybdenum in the ratio of 2 to 3 comes the α-phase modification.

The information presented as supportive evidence for the formation of a heteropoly bismuth molybdate precursor can now be summarized. The octamolybdate seems to be established as existing in the acidified ammonium paramolybdate solution yet it does not seem possible to form a precursor having a bismuth molybdenum ratio of 2 to 3 with this anion. The existence of this polymer does not seem to preclude the existence of another molybdate aggregate which might react with the bismuth as it is added to the acidified molybdate solution similar to results reported on the 12-molybdophosphoric acid system at low pH (*14*). Of importance in this consideration is maintaining an isopoly molybdate that remains constant throughout the preparation. A reaction between the amorphous precipitated molybdate and the added bismuth apparently does occur for a color change of the molybdate precipitate is observed when the bismuth is added. This color change does not occur when simply diluting the acidified molybdate solution with an identical portion of aqueous acid solution. Bismuth can act as a heteroatom. At the pH of mixing, i.e., pH 1.5, the bismuth can precipitate as the hydroxide or a bismuthyl salt. However, preparations involving the bismuth subnitrate appear to give less satisfactory results than those preparations involving the bismuth nitrate. The hydroxyl group can then form a bridge between the bismuth and molybdenum atoms and this heteropoly can be stabilized by ammonia, as observed in polyhydroxy–molybdate complexes (*17*, *18*), or it can use a protonated molybdate isopolyanion, the protons associated with the hydroxyl group of the heteroatom forming hydrogen bridges and thus zeolitic water of hydration. The compound then crystallizes using nonzeolitic water to bind the whole precursor. This heteropoly compound is not amorphous. The intensity line at $d =$ 5.035 Å is one of the characteristic lines of the heteropoly, the relative intensity not being duplicated by other bismuth and molybdenum compounds. However, the stoichiometry of this heteropoly bismuth molybdate precursor has the bismuth to molybdenum ratio of the α-phase. The precursor goes through an amorphous phase before forming the α-phase catalyst. The crystal preceding this amorphism is quite different from the crystal formed after this amorphism. As mentioned, the experimental evidence presented in this work is not sufficient enough to identify exactly the empirical formula of the precursor but does allude to its existence. The same type of precursor, i.e., a bismuth molybdate heteropoly, has recently been suggested by Grzybowska, Haber and Komorek (*19*).

The stability of this heteropoly precursor can be estimated when considering the preparations in which the initial pH of the acidified ammonium paramolybdate solution was allowed to drop from 1.5 to 1.0, and then held constant by back titrating with concentrated aqueous ammonia, preparation 68 of Table 3 for example. This catalyst gave a very good α-phase product, yet the preparations that allowed the mixture to drop below pH 1 during the bismuth nitrate addition, preparations 66 and 67 of Table 3, give poorer catalysts. Thus it seems that pH 1.0 is a lower limit for the coprecipitation method. This conclusion is in agreement with the isopoly molybdate chemistry in which the lower limit of the octamer's existence is about pH 1.1 and is also in agreement with the range of stability of a bismuth–phosphorous-molybdate heteropoly that was observed to be stable over a pH range of 3.2 to 1.0 after which time it dissociated (*20*).

Finally, a stepwise calcination procedure as suggested by Trifiro should result in a better defined crystalline phase. This would be expected because most heteropoly compounds contain both zeolitic and nonzeolitic water. In general, zeolitic water can be removed over a wide range of temperatures from heteropoly compounds without any alteration in the crystal lattice. Nonzeolitic water, on the other hand, is usually lost in a stepwise series of dehydrations. These distinctive steps occur at specific temperatures and usually are associated with crystal structure rearrangement. Obviously, the slow removal of water would result in a slow crystal rearrangement and a more well-defined final phase. Rapid removal of the same water should constitute an explosive change in crystallinity that would not be conducive to an orderly rearrangement and, consequently, would result in poorer crystallinity.

Preparation 101 examined the effect of the heat treatment by treating half of the sample, Part A, to a stepwise calcination and the other half, Part B, to the 2 hr drying followed by 20 hr at 450°C. Table 7 contains the X-ray analysis for this comparison. Although the intensities are rather close with no appreciable quantitative changes, the lines are shifted slightly, the stepwise calcination giving d-spacings of slightly larger magnitudes than Part B. For example, the two most characteristic lines of the α-phase are shifted with Part A's 100% line at $d = 3.191$ Å and 73% line at $d = 3.056$ Å while the same lines for Part B are at $d = 3.184$ Å and $d = 3.053$ Å. In addition, the diffractometer pattern was much better defined for the stepwise calcination.

SUMMARY AND CONCLUSIONS

Two preparations have been shown to give a satisfactory α-phase sample, 112 and 123. The former preparation uses Trifiro's basic coprecipitation procedure modified only so far as to age the precipitate formed. This preparation is limited because of the poor solubility of the bismuth nitrate salt in all but the most acidic solutions. The latter preparation also gives an α-phase catalyst that is reproducibly prepared and is not limited by the solubility of the bismuth nitrate salt in a pH 1.5 solution but is rather limited by the analytical problem of low supersaturation. The following preparation has been shown to give a reproducible α-phase sample: Ninety milligram-atoms of molybdenum [15.8900 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$] are dissolved in 200 cc of water. This solution is acidified to a pH of 1.5 by *slowly* adding an appropriate amount of concentrated nitric acid while vigorously stirring the aqueous molybdate solution. A white precipitate will form. This solution is allowed to stand for 1 hr after acidifying. Sixty milligram-atoms of bismuth [29.1062 g of $Bi(NO_3)_3\cdot 5H_2O$] are dissolved in 30 cc of concentrated nitric acid. After dissolution, the acid solution is distilled with 1170 cc of distilled water. This bismuth nitrate solution is *slowly* added (addition time about 4 hr) to the aged acidified molybdate solution while the latter solution is constantly stirred with an electric stirrer. The temperature of the solutions on mixing should be about 25°C. The pH of the mixture is maintained constant at pH 1.5 by back titrating with concentrated ammonium hydroxide. After the addition is complete the precipitate and mother liquor are allowed to stand for 20 hr. The solution is filtered. The filtrate is used as a wash to clean the glassware and is then passed over the collected precipitate. The precipitate is placed in a crucible and dried at 115°C for 2 hr, calcined at 200°C for 5 hr, and calcined at 450°C for 15 hr.

Based upon the observations of this study, we conclude that:

1. A pure α-phase precipitate can be obtained at a solution pH value of 1.5, but if the solution pH is less than 1.0, impurity phases are obtained;
2. Back titration of the excess acid in the bismuth solution with concentrated NH_4OH is an effective method of maintaining the solution pH at 1.5 during the precipitation;

3. The equilibration of the isopolymolybdate anions during acidification is slow, and therefore, addition of acid to the paramolybdate solution and the addition of the bismuth nitrate solution to the molybdate solution must also be done slowly;
4. The predominate species in solution is suspected to be the octamolybdate anion, and the constancy of its existence during the precipitation appears to be necessary in order to obtain the pure α-phase;
5. Bismuthyl ions are probably not involved in the precipitation step with the molybdate species;
6. The initial precipitate, and the precipitate after drying at low temperatures, is amorphous and is suspected to be a heteropoly bismuth–molybdenum species;
7. Stepwise calcination, as opposed to a single calcination at 450°C, yields a product that has a more clearly defined X-ray pattern.

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