JOURNAL OF CATALYSIS 25, 1-11 (1972)

Bismuth Molybdate Catalysts. Preparation, Characterization and Activity of Different Compounds in the Bi–Mo–O System

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Received March 29, 1971; revised July 27, 1971; accepted October 19, 1971

The influence on oxidation activity of the method of preparation of Bi–Mo catalysts and in particular the circumstances during the wet stage (precipitation, slurry reactions between preprecipitated oxyhydrates) have been investigated. It was found that active Bi/Mo = 2/1 catalysts have to be prepared by a slurry reaction starting from what is essentially $(BiO)(NO_3)$. Even the application of powdered crystals of compounds with this composition leads to active catalysts. Contrary to previous work, active 1/1 catalysts can only be prepared by precipitation but the phase formed is not stable against prolonged heating at temperatures around 500°C.

INTRODUCTION

Bi–molybdate catalysts as applied for the selective oxidation of olefins are usually prepared via some type of precipitation from solutions of NH_4–molybdate and (acidified) Bi–nitrate. The resulting precipitate is subsequently treated at a temperature in the vicinity of 500°C, during which solid state reactions may and do occur. It is often assumed that the composition of the calcined catalyst is ultimately defined by the Bi/Mo ratio and the binary compound consequently formed. Experiments by various workers have shown that this assumption is not altogether satisfactory. For instance, using a slurry type of interaction between preprecipitated Bi-oxyhydrate and Mo–oxyhydrate we found the $Bi_2Mo_2O_9$ (Erman)-phase to be only moderately active while the composition of the commercial acrylonitrile catalyst appears to favor the formation of this compound. One might therefore suppose that the circumstances under which the precipitation or slurry interactions occur might be more important in deciding the ultimate properties of the catalyst than originally supposed. It was the object of this investigation to study this problem. While engaged in it, Haber and co-workers (*1*) informed us about their work on similar lines, while later on we were informed about work by Trifirò *et al.* (*2*) in this connection. Since the results of the three groups appear to fit reasonably well, although approached from different angles, it was considered useful to publish our present results. There are a number of earlier works of importance in this connection (*3–10*).

PREPARATION OF BISMUTH MOLYBDATES

Standard calcination of all materials: 2 hr heating in air at 500°C of sample previously dried at 110°C.

$Bi_2O_3 \cdot MoO_3$

The following solutions were used:

(A) A solution of 150 cm^3 volume from 48.5 g $Bi(NO_3)_3 \cdot 5H_2O$ + 17 cm^3 concentrated HNO_3 and water.

(B) A solution of 8.8 g $(NH_4)_6 \cdot Mo_7O_{24} \cdot 4H_2O$ in 100 cm^3 water.

Precipitation. (1) Solution A was added dropwise to solution B, a white mass being formed at a final pH = 1. The liquid phase in contact with the mass was evaporated and the dried and powdered material calcined. The product was inhomogeneous, containing white, yellow and orange particles.

(2) Solution A was added to solution B, the pH being continuously adjusted around 5 with ammonia with a final pH = 5. After filtration the mass was dried and calcined and a yellow powder was obtained. After evaporation of the filtrate neither Bi nor Mo could be detected in the residue.

(3) This was similar to (2) but during precipitation the pH was adjusted between 7 and 9 after which the liquid phase in contact with the mass was evaporated. During this process we observed further precipitation of ammonium molybdate. The dried powder was calcined.

Reactions of molybdic acid with $Bi(OH)_3$ and with $BiONO_3$. (4) Solution A was added to a large excess of concentrated ammonia solution giving a precipitate with slow filtration properties that was washed with water until ammonia was completely removed. The $Bi(OH)_3$ precipitate, mixed with 8.2 g H_2MoO_4 and 1 liter water, was boiled and stirred for 26 hr. In the beginning a swelling of the mass was observed which slowly disappeared while simultaneously the color of the mass changed from white to yellow. The pH during reaction changed a little, from 7 to 5.

(5) Solution A was added to a diluted ammonia solution and a white precipitate with good filtration properties was obtained which was washed until free from ammonia. The white mass mixed with 8.2 g H_2MoO_4 and 1 liter water was boiled and stirred for 18 hr. The yellow substance was more rapidly formed than in (4) and the pH changed from 7 to 2. After filtration and drying the yellow powder was calcined.

(6) Basic bismuth nitrate (58.4 g of Merck AG quality) containing 79.8% Bi_2O_3 was mixed with 16.2 g H_2MoO_4 and 1 liter water and was boiled and stirred for 18 hr. The yellow substance was rapidly formed and the pH changed from 7 to 2. After filtration and drying the material was calcined.

(7) Powdered crystals of $Bi(NO_3)_3 \cdot 5H_2O$ (48.5 g) were treated with concentrated ammonia solution and after 5 min of stirring the white powder was filtered and washed until free from ammonia. The powder, mixed with 8.2 g H_2MoO_4 and 1 liter water, was boiled and stirred for 18 hr. The pH changed from 7 to 2 and a yellow powder was rapidly produced. After filtration and drying it was calcined. In experiments 5, 6 and 7 no swelling effects were observed. Needles obtained after evaporation of the water filtrates in experiments 4, 5, 6 and 7 were identified as being NH_4NO_3. They are formed because commercial molybdic acid contains a small amount of ammonium molybdate and NH_4NO_3 may originally be present as contamination of the $Bi(OH)_3$ and $BiONO_3$ precipitates. In all the experiments the final weight of the catalysts corresponded with 0.05 g mol $Bi_2O_3 \cdot MoO_3$ except sample (6) for which the final weight was 0.01 g mol $Bi_2O_3 \cdot MoO_3$.

$Bi_2O_3 \cdot 3MoO_3$

(8) A solution of 13.2 g $(NH_4)_6 \cdot Mo_7O_{24}$ $4H_2O$ in 100 cm^3 water was added dropwise to a solution of 24.2 g $Bi(NO_3)_3 \cdot 5H_2O$, 9 cm^3 concentrated HNO_3 and 90 cm^3 water and a white precipitate was obtained. After evaporation a white material was formed which after drying and calcination turned into a slightly yellow colored powder.

(9) This was similar to (4) but now a large excess (150 g) of H_2MoO_4 was used. During boiling and stirring a strong swelling of the mass was observed and the color remained white. After 20 hr reacting time the mass was filtered, dried and calcined. Then it was treated with a large excess of warm concentrated ammonia solution to remove excess MoO_3. The white powder was washed with water to remove ammonia and was calcined again. The weight of the white colored catalyst corresponded to 0.05 g mol $Bi_2O_3 \cdot 3MoO_3$.

$Bi_2O_3 \cdot 2MoO_3$

The following solutions were used:

(C) A solution of 100 cm^3 volume from 24.2 g $Bi(NO_3)_3 \cdot 5H_2O$, 9 cm^3 concentrated HNO_3 and water.

(D) A solution of 8.8 g $(NH_4)_6 \cdot Mo_7O_{24}$ in 100 cm^3 water.

(10) Solution D was added to solution C

and a white precipitate was obtained. The final pH of 1 was adjusted with ammonia to 5 and after filtration, washing and drying, the white powder was calcined. After evaporation of the filtrate we could not observe Bi or Mo compounds in the residue. By treating part of the catalyst sample with ammonia, 2 wt% MoO_3 could be extracted. Another part of the sample calcined at 500°C was further heated at 450°C for 90 hr during which the color of the sample changed from white to yellow.

(11) Solution C was added to solution D. Because of intermittent addition of ammonia the pH during precipitation fluctuated between 6 and 3 with a final pH of 5. After filtration, washing and drying, the white powder was calcined. No loss of Bi or Mo material was observed.

(12) This followed the same procedure as (10) but instead of direct filtration we boiled and stirred the mass for 10 hr during which we observed a change of color from white to slightly yellow. After filtra-

TABLE 1

X-RAY DATA (d-VALUES IN Å AND RELATIVE INTENSITIES) OF SAMPLES WITH A Bi/Mo = 2/1-RATIO

exp-1		exp-2		exp-3		exp-4		exps-5-6-7	
8.140	15	8.192	20	8.12	26	8.046	16	8.20	10
6.970	5								
6.674	3								
6.308	4								
5.943	4					5.650	5		
4.919	8	4.553	4	4.55	4			4.55	2
4.529	5					4.529	4		
3.790	9	3.786	8	3.78	8	3.769	8	3.79	4
3.557	5					3.258	91		
3.201	50	3.209	22			3.190	18		
3.164	100	3.164	100	3.16	100	3.155	100	3.165	100
3.061	14								
2.885	10					2.876	16		
2.799	11	2.813	6			2.799	20		
2.755	38	2.755	48	2.75	50	2.749	41	2.76	25
2.705	34	2.708	30			2.701	34	2.71	17
				2.67	45				
2.607	5	2.622	6	2.605	6	2.600	5	2.61	3
2.492	15	2.494	16	2.597	6				
		2.429	4	2.489	20	2.488	14	2.494	8
2.276	5	2.276	5	2.425	4	2.423	2	2.430	2
				2.271	6	2.270	6	2.277	3
						2.005	16		
1.993	8					1.977	11		
1.949	28	1.946	28	1.942	33	1.942	32	1.945	15
1.925	30	1.929	38	1.926	48	1.929	42	1.929	22
1.888	6	1.891	4	1.888	5	1.891	3	1.890	2
				1.783	2			1.786	1
				1.778	2				
				1.730	3			1.729	1
				1.726	2				
				1.723	2				
				1.682	5				
				1.654	42			1.655	20
				1.582	33			1.638	16
				1.578	20			1.580	10
				1.574	16				

tion and drying the powder was calcined. No loss of material was observed.

(13) Solution C was added to solution D. By adding ammonia the pH was maintained between 9 and 7. After evaporation the dried powder was calcined and a yellow material was obtained. Evaporation here is necessary because a filtration procedure even at pH = 5 will give loss of material in the form of dissolved ammonium molybdate.

X-Ray Measurements

Results were obtained with a Philips X-ray diffractometer with Geiger–Müller counter and Ni-filtered CuK_α radiation. The results are given in Tables 1–3. The pattern of lines chosen as characteristic for the various compounds were obtained from Erman *et al.* (*8*), Batist *et al.* (*3*) and Aykan (*6*), as follows:

TABLE 2

X-RAY DATA (d-VALUES AND INTENSITIES) OF SAMPLES WITH Bi/Mo = 2/3 RATIOS AND OF PREPARED U.S.P 2.904.580 CATALYSTS

exp-8		exp-9		U.S.P 2.904.580 calc. 560°C		U.S.P 2.904.580 calc. 720°C	
8.08	12	7.893	9	6.62	vw	4.84	vw
6.96	3	6.975	16	5.94	vw	3.20	vw
6.74	6	6.289	8	4.90	vw	3.151	100
5.90	3	5.968	2	3.20	50	3.083	40
5.29	3	5.760	2	3.153	100	2.942	50
5.09	5	5.410	6	2.936	15	2.639	50
4.90	13	5.083	5	2.915	vw	2.554	vw
4.55	3	5.029	2	2.812	15	2.313	16
3.97	12	4.902	32	2.642	15	1.154	vw
3.78	7	4.567	11	2.453	vw	1.961	48
3.60	13	4.440	1	2.290	vw	1.957	45
3.54	35	3.759	6	2.184	vw	1.864	30
3.46	10	3.616	9	1.957	22	1.737	28
3.26	7	3.594	14	1.866	10	1.730	30
3.19	65	3.487	1	1.731	12	1.604	40
3.16	100	3.429	12	1.689	11	1.573	22
3.05	23	3.336	10	1.641	7		
2.98	9	3.272	19	1.609	vw		
2.87	12	3.191	100	1.601	16		
2.80	13	3.058	85				
2.79	15	2.993	1				
2.75	25	2.879	35				
2.69	24	2.795	19				
2.66	13	2.762	3				
2.57	6	2.661	4				
2.48	12	2.638	3				
2.00	8	2.582	2				
1.94	23	2.542	1				
1.92	24	2.510	7				
1.88	10	2.486	15				
1.65	12	2.445	2				
1.63	16	2.348	3				
1.58	9	2.324	6				
		2.296	3				
		2.279	5				
		2.248	15				
		finished at 40°28″					

TABLE 3

X-Ray Data of Samples With Bi/Mo = 1/1 Ratio

(d-Values and Relative Intensities)

exp-10		exp-11				exp-12		exp-13		(10)-90 hr-450°C	
8.01	20	8.11	40			8.22	20	8.16	15	8.11	13
6.67	35	6.96	15			7.06	18	7.92	13	7.89	5
5.94	45	6.65	30			6.36	8	6.99	32	6.97	10
5.21	30	6.30	10			5.45	8	6.31	12	6.30	5
4.92	70	5.94	40			4.94	25	6.00	5	5.41	3
4.78	45	5.42	10			4.59	20	5.77	5	5.08	2
4.55	8	5.21	20			3.81	12	5.42	10	4.93	40
4.22	10	4.92	75			3.64	15	4.92	55	4.58	15
3.91	20	4.78	33			3.46	10	4.58	20	3.78	13
3.78	40	4.55	15			3.39	8	3.93	10	3.60	15
3.57	10	4.22	6			3.28	25	3.63	13	3.42	13
3.44	5	3.91	15			3.20	160	3.61	22	3.33	10
3.30	30	3.78	42			3.16	250	3.44	16	3.27	28
3.20	600	3.60	13			3.08	95	3.43	10	3.19	135
3.15	400	3.56	8			2.90	40	3.34	16	3.16	250
3.06	40	3.43	10			2.79	27	3.28	40	3.06	100
2.98	20	3.34	5			2.76	75	3.19	180	2.88	43
2.87	20	3.31	7			2.71	27	3.15	120	2.79	28
2.81	100	3.26	25			2.61	6	3.06	100	2.75	65
2.73	30	3.21	600			2.499	36	2.89	56	2.70	40
2.70	100	3.15	400			2.366	5	2.80	35	2.60	8
2.59	5	3.06	100			2.330	4	2.75	45	2.51	10
2.55	5	2.98	13			2.285	10	2.70	17	2.49	35
2.486	5	2.88	45			2.258	12	2.51	12	2.44	3
2.456	12	2.81	100			2.194	5	2.487	32	2.42	6
2.384	5	2.72	95			2.133	20	2.359	6	2.35	3
2.319	5	2.70	100			2.008	25	2.325	8	2.32	8
2.276	5	2.66	10			1.951	42	2.277	12	2.27	10
2.254	5	2.60	15			1.934	72	2.252	16	2.19	15
2.194	30	2.55	10			1.888	30	2.184	5	2.18	3
2.176	35	2.487	45			1.852	10	2.137	7	2.12	3
2.142	8	2.321	10			1.809	10	2.123	8	2.09	5
2.043	20	2.265	20			1.776	6	2.097	8	2.06	5
1.992	70	2.225	20			1.773	18	2.008	32	2.02	5
1.986	65	2.197	20			1.699	25	1.962	25	2.00	25
1.982	70	2.176	25			1.659	60	1.927	38	1.96	10
1.945	100	2.043	10			1.638	48	1.916	25	1.94	38
1.928	30	1.994	47			1.597	18	1.888	30	1.93	58
1.883	20	1.980	47			1.581	30	1.850	10	1.88	28
1.852	8	1.946	100	1.654	72	1.534	15	1.806	16	1.85	8
1.806	1	1.928	82	1.637	95			1.767	10	1.84	5
1.773	15	1.883	27	1.604	30			1.712	20	1.83	5
1.729	5	1.847	10	1.598	45			1.698	25	1.80	5
1.687	100	1.804	15	1.588	40			1.657	32	1.78	3
1.653	30	1.773	12	1.557	10			1.654	33	1.73	8
1.641	95	1.729	10	1.530	10			1.635	30	1.73	8
1.597	65	1.717	10					1.597	15	1.71	15
1.584	20	1.689	100					1.594	16	1.70	18
		1.686	100					1.578	17	1.65	48
								1.555	9	1.63	35
										1.59	10
										1.58	23

2/1 (koechlinite)

d = 8.04, 3.15, 2.74 and 2.69, 1.940 and 1.926, 1.655 and 1.630, 1.575.

1/1 (Erman)

d = 5.95, 4.90 and 4.74, 3.20 and 3.15, 2.80 and 2.70. 1.990, 1.978 and 1.940, 1.682 and 1.638, 1.598.

2/3

d = 6.90, 4.89, 3.57, 3.26 and 3.18, 3.05 (most characteristic), 2.87 and 2.79, 2.005, 1.915, 1.690.

Bi/Mo = 2/1. (Table 1, relative intensities with reflection = 100) Sample 1 is a mixture containing koechlinite and $Bi_2O_3 \cdot 3MoO_3$. Sample 2 is predominantly koechlinite with perhaps some 1/1, while sample 3 is also mainly koechlinite. Sample 4 contains koechlinite but with appreciable amounts of another compound (perhaps low temp. Bi_2O_3). Samples 5, 6 and 7 are very similar and show almost no reflections except those of koechlinite. An interesting detail, however, is the different intensity ratio of the koechlinite lines in the group 1–4 on the one hand and 5–7 on the other, the 3.15 line being much stronger in the second group.

Bi/Mo = 2/3. (Table 2, which contains also the data for the Bi–P–Mo catalysts) Sample 8 is a mixture of the 2/3 and 2/1 compounds while sample 9 is almost pure 2/3 with a pattern completely similar to that of Aykan (*6*). The 560°C preheated technical catalyst approximates to the 1/1-phase although in the X-ray diagram there remain some unidentified lines. The 720°C preheated sample is characterized by a diagram similar to that given by McClellan (*7*).

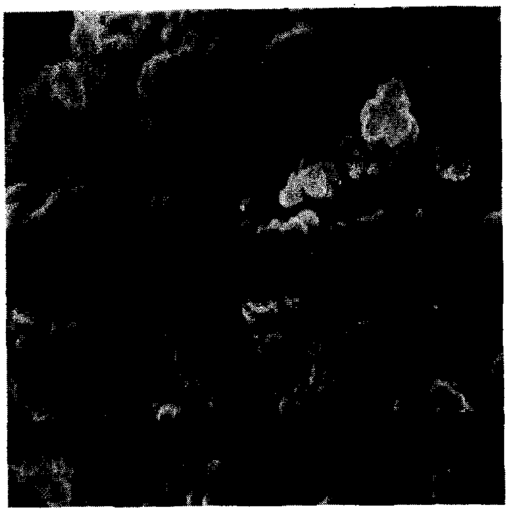
Bi/Mo = 1/1. (Table 3, intensities as observed) Sample 10 produces a diagram similar to that given by Erman *et al.* (*8*) for the 1/1 phase but the 2/3 and 2/1 compounds are also present. However, sample 10 (calcined 90 hr at 450°C) shows hardly any 1/1-lines and is a mixture of 2/3 and 2/1. A completely similar pattern is obtainable from a mixture of 0.01 g mol of sample 9 and 0.01 g mol of sample 7. Sample 11 is similar to 10 but with greater concentrations of 2/3 and 2/1. Samples 12 and 13 are predominantly mixtures of 2/3 and 2/1.

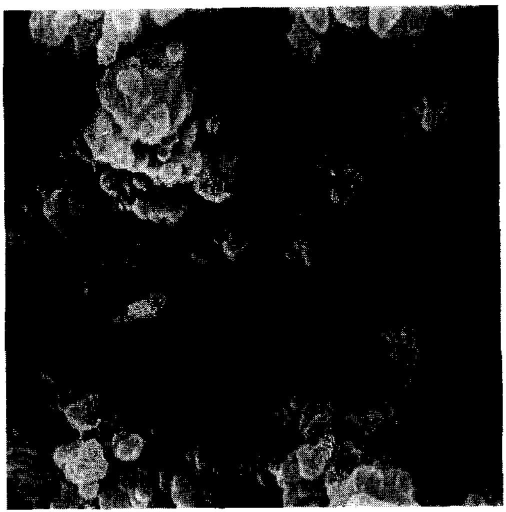
Stereoscan Photographs

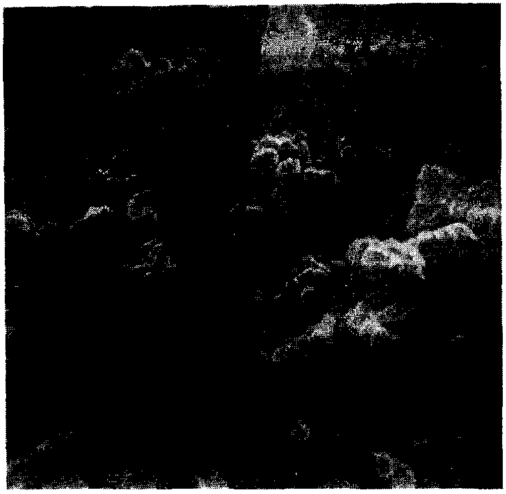
Some photographs were made with a Stereoscan MK IIA microscope using the emissive mode technique. Powdered samples of some 2/1 catalysts were first impregnated with antistatic (Mirasol) and subsequently embedded in Leitsilber to attach them on the specimen stub, covered with a carbon layer and finally with the conducting gold layer. Specimen tilt 45° and magnification of 10500 were used. Only photographs of samples 3, 4 and 7 are given (Plates 1–3). All specimens of 2/1 samples show conglomerations of globular particles (dimension on the average 10^{-4} cm). Samples 3 and 7 show differences in the packing of these particles; the packing in 3 is appreciably denser (surface areas of the two samples 4.8 and 4.1 $m^2\, g^{-1}$, respectively). Only specimen 4 shows a noteworthy detail: apart from the usual globules there seem to occur larger crystals of a different type. (This is not a Leitsilber crystal as shown by Plate 4, which is a photograph of the border of a specimen stub with some isolated particles on Leitsilber.) The surface area of this sample is significantly lower (1.7 $m^2\, g^{-1}$).

Activity Tests for 1-Butene Oxidation

In each experiment a microreactor was filled with 750 mg of catalyst and a continuous feed of 20 $cm^3\, min^{-1}$ 1-butene and 100 $cm^3\, min^{-1}$ artificial air was brought into contact with the catalyst at a temperature of 438°C. Butene to butadiene conversions in Table 4 show that precipitated Bi/Mo = 2/1 catalysts (sample 1 and 3) are less active. Only sample 2 shows a moderate activity. The best results for the Bi/Mo = 2/1 catalysts are obtained with the samples 5, 6 and 7 which were made by the new procedure. Sample 4 is lower in its activity. Further it is shown that the precipitated Bi/Mo = 2/3 catalyst and the catalyst made by the new procedure are less active. However, sample 8 containing a small amount of koechlinite is a little more active than sample 9. Finally it is







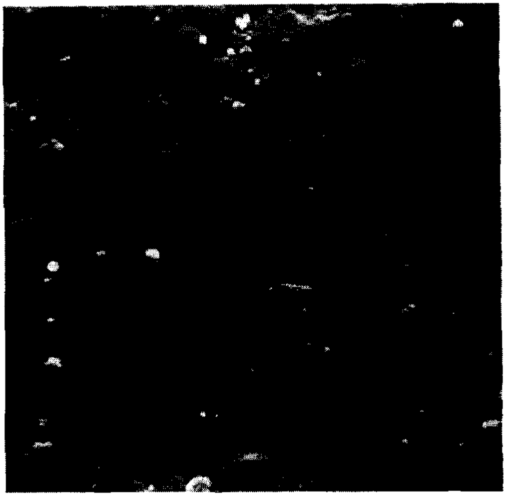


Plate 1. Stereoscan photograph of $Bi_2O_3 \cdot MoO_3$, Sample 3. ×10,500.
Plate 2. Stereoscan photograph of $Bi_2O_3 \cdot MoO_3$, Sample 4. ×10,400.
Plate 3. Stereoscan photograph of $Bi_2O_3 \cdot MoO_3$, Sample 7. ×11,000.
Plate 4. Stereoscan photograph of Leitsilber. ×4850.

shown that the precipitated Bi/Mo = 1/1 catalysts (samples 10–13) are comparable to the koechlinite samples 5, 6 and 7 with respect to their activities; moreover their selectivities are somewhat superior. The supported Bi–P–Mo catalyst, calcined at 560°C, was also active. The same catalyst, calcined at 720°C, was less active (no data in Table 4). Samples 6 and 10 were further investigated by using smaller amounts with the same feed as mentioned above. Both catalysts are more selective the shorter the contact time and optimum results with respect to the selectivity are obtained with 350 mg of catalyst (see Table 5). In one run one obtains 75% butadiene at temperatures around 460°C and the selectivities with respect to total combustion, expressed by the ratio: diene/(diene + CO_2), surpass the value of 93%. From our data we calculated the Arrhenius plots by assuming a first order dependency on the butene pressure and a zero order dependency on the oxygen pressure. The results for samples 6 and 10, together with those for the Bi–P–Mo catalyst supported on silica, are represented in Fig. 1.

For the three different types of catalyst

TABLE 4

CATALYTIC ACTIVITIES FOR OXIDATION OF 1-BUTENE. GAS COMPOSITION (%) (ON C-BASIS) AFTER OXIDATION ON 750 MG OF CATALYSTS WITH A FEED OF 20 $\text{CM}^3\ \text{MIN}^{-1}$ 1-BUTENE AND 100 $\text{CM}^3\ \text{MIN}^{-1}$ ARTIFICIAL AIR AT A REACTION TEMPERATURE OF 438°C (CATALYST NUMBER EQUAL TO EXPERIMENT NUMBER OF PREPARATION)

Cat	Bi/Mo			2-butene		
#	ratio	CO_2	1-butene	*trans*	*cis*	butadiene
1	2/1	2.0	72.5	1.1	1.1	23.3
2	2/1	2.6	44.4	1.4	4.8	46.8
3	2/1	2.6	70.1	0.7	1.1	25.6
4	2/1	2.1	31.0	5.9	7.0	54.0
5	2/1	8.4	8.4	5.6	4.2	73.4
6	2/1	10.4	9.7	5.2	4.4	70.1
7	2/1	4.5	16.4	5.9	5.2	68.0
8	2/3	0.8	68.7	2.5	3.4	24.6
9	2/3	0.3	89.3	0.3	0.5	9.6
10	1/1	4.1	16.4	5.9	6.5	67.1
11	1/1	3.9	15.3	5.3	6.9	68.6
12	1/1	2.3	24.5	3.7	3.0	65.0
13	1/1	1.3	29.6	3.8	3.8	61.5

Data obtained from single experiment.

it is shown that the activation energies in the low range of temperatures are of the same order of magnitude (33 kcal mole^{-1}). At the higher reaction temperatures all catalysts show a tendency to smaller activation energies (*ca.* 10 kcal mole^{-1}). Because of the similarity shown in the Arrhenius plots for the three different catalysts we also investigated the supported Bi–P–Mo catalyst. In Fig. 2 the conversion of butenes as function of catalyst weight is represented and it is shown that already good conversions are obtainable at short contact times. Inhibition by butadiene can also be observed from this figure where it is shown that the butene conversion becomes almost zero when butadiene is added to the feeds of butene and artificial air.

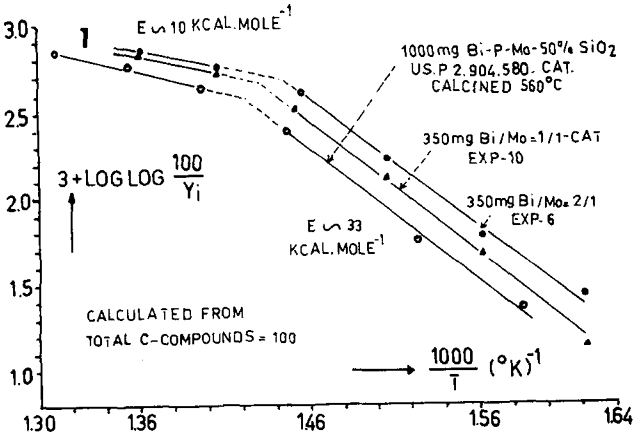
Reaction kinetics, i.e., the order dependencies, are represented in the next figures.

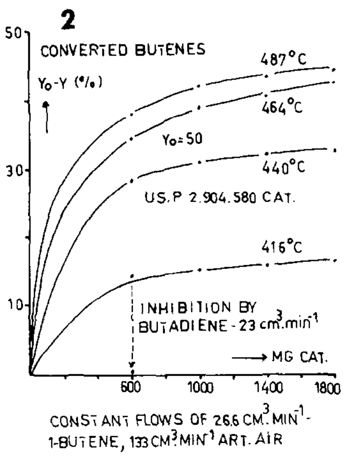
TABLE 5

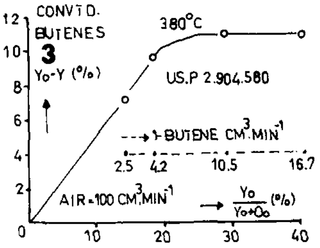
GAS COMPOSITION AFTER 1-BUTENE OXIDATION (ON C-BASIS) AS FUNCTION OF REACTION TEMPERATURE (°C) FOR 350 MG OF THE Bi/Mo = 2/1 AND 1/1 CATALYSTS

Temp. (°C)	Catalyst	CO_2	1-butene	*trans*	*cis*	diene	total butenes Y_i
343	(2/1)	0.5	92.2	0.7	0.7	5.7	93.6
	(1/1)	0.3	92.7	1.0	1.1	4.9	94.8
367	(2/1)	1.1	84.6	1.1	1.5	11.8	87.1
	(1/1)	1.0	83.6	2.6	3.0	9.8	89.2
391	(2/1)	1.7	60.6	2.9	3.6	31.1	67.1
	(1/1)	1.4	64.2	4.4	5.0	25.0	73.6
415	(2/1)	4.8	27.8	5.9	5.1	56.4	37.8
	(1/1)	1.3	29.6	8.5	8.9	51.7	47.0
438	(2/1)	5.0	14.2	5.2	6.7	67.6	26.1
	(1/1)	2.5	14.8	7.2	7.8	67.7	29.8
462	(2/1)	5.3	8.4	6.1	5.2	74.8	19.8
	(1/1)	2.8	9.1	6.5	6.2	75.4	21.8

Data obtained from double and triple experiments.







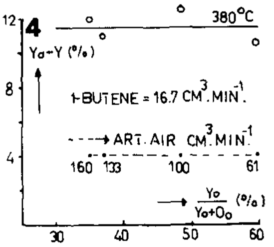


FIG. 1. Activity pattern in the form of Arrhenius plots for the 3 different types of catalyst.

FIG. 2. Influence of contact time on butene conversion and the inhibition of the oxidation by butadiene.

FIG. 3. Deviation of the first order dependence on butene pressure.

FIG. 4. The zero order dependency on oxygen pressure.

Figure 3 shows a deviation from the first order dependency on the butene pressure, an effect which is caused by diene inhibition. Figure 4 shows that within certain limits the oxidation is zero order with respect to the oxygen pressure. It should be mentioned that Fig. 1 is obtained from data of gas composition in which only carbon-containing compounds are considered. The converted butenes in Figs. 2, 3 and 4 are calculated from gas compositions in which steam and oxygen values are included (see our previous report (*11*)). Finally it should be noticed that the reaction time during which the catalysts were tested for activity was a couple of hours so that the effect of thermal decomposition of the 1/1-phase was minimal.

DISCUSSION

Consider first the samples 4–7 which are prepared according to our usual technique of wet slurry interactions. In sample 4 great care was taken to remove NO_3^- ions from the precipitate so as to obtain it in the (BiO)(OH) form, the resulting catalyst after interaction of Bi-oxyhydrate with molybdic acid being only moderatively active. From the stereoscan photograph the impression is gained that the reaction in the wet phase between the slurry components was not complete (presence of larger crystals, low surface area). In sample 5 a diluted ammonia solution was used and the precipitate obtained probably still contained appreciable quantities of NO_3^- ions; see the change in pH from 7 to 2 after interaction with molybdic acid. This catalyst sample proved very active, leading to the supposition that active catalysts of composition 2/1 have to be prepared from what is essentially (BiO)(NO_3). Sample 6 prepared from powdered basic bismuth nitrate without further precipitation, again furnishing an active catalyst, proved this assumption to be correct. Even ammonia treated powdered Bi-nitrate is sufficient to arrive at an active catalyst (sample 7). We therefore postulate that active catalysts of the Bi/Mo = 2/1 composition arise out of a reaction such as:

$$2(BiO)(NO_3) + H_2MoO_4 \rightarrow (BiO)_2MoO_4 + 2HNO_3 \quad (1)$$

It is noteworthy in this connection that the intensity ratios of the lines in the koechlinite diagram were different in the active samples from those in the samples with lower activity, the d = 3.15 line being much more developed relative to the others as in sample 4. This may possibly be explained from a pseudomorphism of the resulting koechlinite crystals with respect to basic Bi-nitrate.

Precipitation of 2/1 samples from solutions of acidified Bi-nitrate and ammonium molybdate appears a less appropriate method to arrive at active samples (see 1–3). This is partly due to incomplete precipitation of the components of the koechlinite compound (see for instance sample 1 which contains $Bi_2O_3 \cdot 3MoO_3$), partly to the fact that the crystal structure obtained is less favorable (intensity ratios of lines in X-ray diagram different from those in the active samples), partly perhaps also to a closer packing of the globular koechlinite particles (see stereoscan of sample 3). As for the 2/3 compound, simple precipitation does not lead to a pure sample: there is always some 2/1 present (sample 8). A pure 2/3 compound (sample 9) can be prepared by the method of separate precipitation of the Bi-oxyhydrate and subsequent prolonged boiling with excess molybdic acid. The latter sample, after removing the excess MoO_3, is only slightly active.

Commercial catalysts are usually prepared with a Bi/Mo ratio between 2/3 and 1/1. The 3/4 catalyst approximated in its X-ray diagram to the 1/1 catalyst and was indeed much more active than the pure 2/3 phase. This to us was rather surprising since according to our earlier findings the 1/1 phase was only moderately active (surface area = 1 $m^2 g^{-1}$). Haber and coworkers (*1*) on the one hand and Trifirò and coworkers (*2*) on the other hand have since reported that the 1/1 compound can be formed by precipitation from solutions of Bi-nitrate and NH_4-molybdate and that the compound exists at temperatures below 560°C. From our experiments starting from the slurry interaction method we never observed its formation at lower temperatures and only found it to be formed at temperatures above 560° and below 620°C (see (*3*)). The results of the authors mentioned above now have been confirmed: it appears that precipitation from mixed solutions does indeed lead to considerable amounts of the 1/1 phase being present in the 500°C preheated samples (see samples 10, 11). The samples were found to be of excellent activity. Consequently, precipitation from solution of Bi-nitrate and NH_4-molybdate appears to be the correct method to obtain the 1/1 compound in an active state. However, it was also found that the compound is inherently unstable below 560°C. Heating for 90 hr at 450°C decomposes it into 2/3 and 2/1. Even boiling the precipitate appears sufficient to destroy it (sample 12). Hence, even if it had been formed initially in the solid state reaction between (BiO)(NO_3) and molybdic acid it could not have survived the boiling of the slurry. It is interesting to observe that the activity of the decomposed 1/1 sample is high and therefore presumably contains the koechlinite modification in its active form (40% of catalyst weight in the koechlinite modification). Figure 5 gives a summary of the genetic connections in the formation of the Bi/Mo catalysts following the conclusions formulated above. One interesting observation is that the oxidation kinetics for the

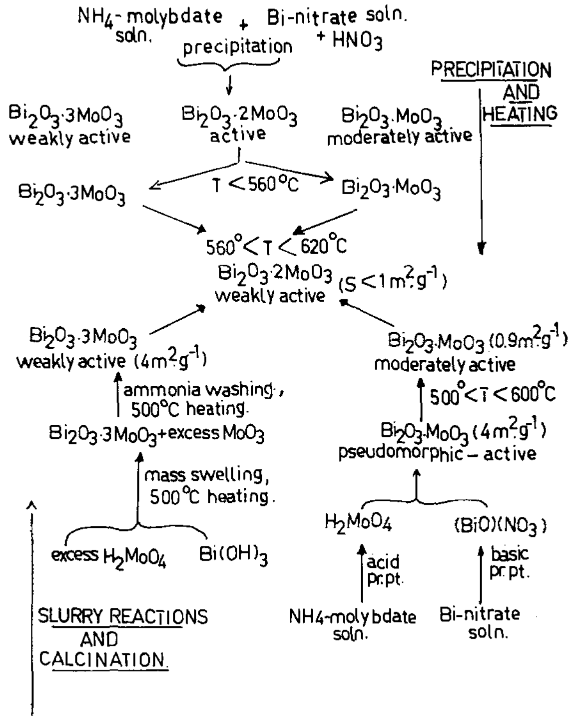


Fig. 5. Summary of genetic connections between various phases in the Bi_2O_3–MoO_3 system.

various types of catalyst are very similar, thus leading to the conclusion that the active sites are similar in all cases. To check this, experiments on the adsorptive properties of the 1/1 and commercial catalysts have been carried out by Matsuura in our laboratory. They will be reported in a later paper together with the redox and sintering properties of these catalysts.

Acknowledgments

Thanks are due to Professor Dr. G. Rieck and Dr. K. Koopmans for putting X-ray facilities at our disposal and to H. P. J. Jongeneelen for investigating kinetics. We gratefully acknowledge the cooperation of Dr. F. A. Schneider and Miss M. H. A. Blylevens for preparing the stereoscan photographs.

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