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Stability Aspects and Olefine Adsorption Properties of $Bi_2Mo_2O_9$ and of the Silica-Supported $Bi_9PMo_{12}O_{52}$ Catalyst

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The adsorption of 1-butene and butadiene on $Bi_2Mo_2O_9$ and on silica-supported $Bi_9PMo_{12}O_{52}$ catalyst was measured. Both catalysts (in which the Erman phase is the major component) show weak single-site adsorptions of 1-butene and butadiene and a slow but strong adsorption of butadiene.

Thermal decomposition of the Erman phase into $Bi_2O_3{\cdot}3MoO_3$ and $Bi_2O_3{\cdot}MoO_3$ runs parallel with a change of the weak single-site type of adsorption into a dual-site type of adsorption, well known as belonging to the koechlinite phase. The silica-supported catalyst is thermally more stable than the $Bi_2Mo_2O_9$ compound. The supported catalyst is found to be partially unstable if exposed to reduction–reoxidation conditions at 470°C. Suggestions are given as to the role of P in silica-supported Bi–Mo catalyst.

INTRODUCTION

In our previous studies of the selective oxidation of 1-butene over bismuth molybdates, most attention was given to the properties of the $Bi_2O_3{\cdot}MoO_3$ compound, the koechlinite catalyst. Reduction–reoxidation reactions (*1*) were carried out under varying conditions, and activities and selectivities were connected with the layer structure of this compound (*2*, *3*) leading to diffusion models for oxygen in the solid. Adsorptions of various reactants and products were studied (*4*) in which it was proposed that the surface contained two types of sites, viz, a site for the adsorption of 1-butene (B-center) and a site for the adsorption of butadiene (A-center). A surface site model for selective olefine oxidations (*5*) was proposed that explains the rather peculiar kinetics observed with this catalyst.

Less attention was so far given to the $Bi_2Mo_2O_9$ catalyst and to the silica-supported $Bi_9PMo_{12}O_{52}$ catalyst (prepared according to USP 2.904.580). We reported only [see (*6*)] that: (a) both catalysts contained considerable amounts of the phase first discovered by Erman *et al.* (*7*); (b) they showed excellent activities and selectivities for the butene oxidation reaction, (c) the kinetics were similar to the kinetics observed for the koechlinite catalyst; (d) $Bi_2Mo_2O_9$ is thermally unstable (*8*) and decomposes into the congruent $Bi_2O_3{\cdot}3MoO_3$ and $Bi_2O_3{\cdot}MoO_3$ compounds during prolonged heating between 450 and 500°C.

The present paper deals in the first instance with olefin adsorptions on $Bi_2Mo_2O_9$ and on the SiO_2–$Bi_9PMo_{12}O_{52}$ catalyst. There are, however, some other aspects which make further studies necessary. One interesting question is whether SiO_2–$Bi_9PMo_{12}O_{52}$, known to contain $Bi_2Mo_2O_9$, is thermally stable or not. Another important question is the behavior of the SiO_2–$Bi_9PMo_{12}O_{52}$ catalyst if it is exposed to reduction–reoxidation conditions: Bouwens in our laboratory has recently shown that $Bi_2Mo_2O_9$ completely decomposes during extensive reduction with 1-butene followed by a complete reoxidation.

Finally, we have the problem of the role of phosphorus in the silica-supporthed $Bi_9PMo_{12}O_{52}$ catalyst. The formula as written here for the composition creates the impression that compound formation could be based on a combination of BiO^+ ions and phosphomolybdate ions, as present in the heteropolyacid $P_2O_5 \cdot 24MoO_3 \cdot 30H_2O$. We have therefore tried to synthesize a Bi-compound of phosphomolybdic acid.

The present studies were greatly facilitated by a cooperation with the Physical Chemistry Department of the University of Eindhoven, where Van den Elzen and Rieck have started a study of the structures of the different bismuth molybdates (*9*). In this paper we hope to show that a correlation exists between the results of olefin adsorptions and of X-ray studies.

For the sake of completeness some adsorption properties of the pure $Bi_2O_3 \cdot 3MoO_3$ compound also will be given; preparation of this selective but moderately active catalyst is described in an earlier paper (*6*) (Expt No. 9).

EXPERIMENTAL PROCEDURE

A. Olefin Adsorptions

The technique of measuring these adsorptions on Bi–Mo catalysts in a classical adsorption apparatus has been described by Matsuura and Schuit (*4*, *5*).

B. Preparation of $Bi_9PMo_{12}O_{52}$

A 4.35 sample of phosphomolybdic acid crystals $P_2O_5 \cdot 24MoO_3 \cdot 30H_2O$ (containing, by analysis, 16.4 wt% H_2O) was dissolved in 50 cm³ water and a yellowcolored solution was obtained. A 9.19 g sample of $Bi(NO_3)_3 \cdot 5H_2O$ crystals, mixed with 4.5 cm³ concentrated nitric acid, were dissolved in warm water to a final volume of the solution of 30 cm³. This solution was added dropwise to the phosphomolybdic acid solution. After adding 10 cm³ of the Bi-nitrate solution a deposit was formed; the mother liquor, however, was still yellow, indicating that precipitation was not complete. By adding further Bi-nitrate solution to the mixture it turned out that 30 cm³ was necessary to obtain a complete precipitate, the liquid now being colorless. This means that complete precipitation occurs at the atomic Bi/Mo ratio of 3/4. After filtration and drying, the powder so obtained was calcined at 500°C for 2 hr.

C. X-Ray Measurements

Data were obtained with a Philips X-ray diffractometer with argon filled proportional counter and Ni-filtered Cu $K\alpha$ radiation. The pattern of lines chosen as characteristic for the various compounds were obtained from Erman *et al.* (*7*), Batist, Bouwens and Schuit (*6*), Aykan (*10*), and Van den Elzen (*9*). The following samples were analyzed:

1. The nonsupported $Bi_9PMo_{12}O_{52}$ catalyst (prepared as shown above).
2. The silica-supported $Bi_9PMo_{12}O_{52}$ catalyst after further calcinations. For testing the thermal stability, samples of the fresh catalyst (calcined at 560°C) were further heated in air, one sample for 50 hr at 500°C and another for 20 hr at 600°C.
3. The silica-supported $Bi_9PMo_{12}O_{52}$ catalyst after redox reactions. For testing the redox stability the following procedure was applied. During a period of 50 hr we subjected 1500 mg of fresh catalyst at 470°C to redox conditions in a microreactor in which 1-butene (20 cm³ min^{-1}) was oxidized to butadiene with 100 cm³ min^{-1} of air. Samples after 26 hr and after 50 hr reaction were obtained, their activities being equal to that of the fresh catalyst.
4. A sample of spent catalyst after 1 yr of ammoxidation of propene in a fluid bed reactor was available, the catalyst being less active than the fresh catalyst.

EXPERIMENTAL RESULTS

A. Adsorption Measurements

Figure 1 shows the adsorption of 1-butene on $Bi_2Mo_2O_9$ and on the silica-supported $Bi_9PMo_{12}O_{52}$. For both catalysts we found a weak single-site type of adsorption, the heat of adsorption being 12 kcal mole^{-1}. The total volume of adsorption is 0.2 cm³ g^{-1}. Because of the composition of the supported catalyst (50 wt% SiO_2) the total amount of adsorption per gram on $Bi_9PMo_{12}O_{52}$ is twice that on $Bi_2Mo_2O_9$. Figure 2 (left) shows a weak single-site adsorption of butadiene on both catalysts, the heat of adsorption being 10–11 kcal mole^{-1}, the total amount of ad-

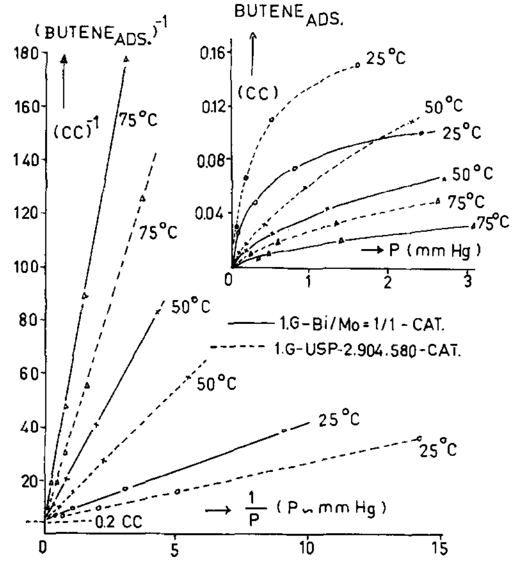

FIG. 1. Weak single-site type of adsorption of 1-butene on $Bi_2Mo_2O_9$ and on silica-supported $Bi_9PMo_{12}O_{52}$ (USP 2, 904,580).

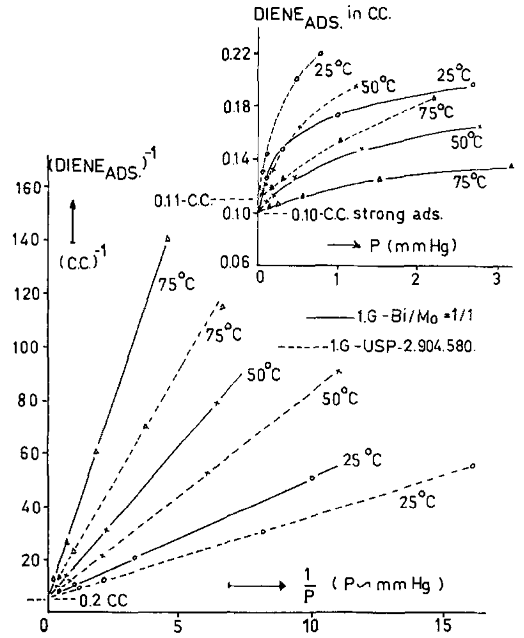

FIG. 2. (left) Weak single-site adsorptions of butadiene on $Bi_2Mo_2O_9$ and on SiO_2–$Bi_9PMo_{12}O_{52}$. (right) Strong adsorption of butadiene on these catalysts.

sorption for $Bi_2Mo_2O_9$ again being 0.2 cm^3 g^{-1} and for $Bi_9PMo_{12}O_{52}$ two times higher. Figure 2 (right) shows a strong adsorption of butadiene on both catalysts. Desorption of butadiene was found to be accompanied by oxidation; as a consequence, it proved impossible to ascertain its characteristics except for the maximum volume adsorbable. The impression is gained that the heat of adsorption is larger than for Bi_2MoO_6, which agrees with some details in the butene oxidation kinetics [see (*6*)]. This behavior, i.e., desorption accompanied by oxidation, is further denoted as "irreversible."

Figure 3 (left) shows the decrease of the

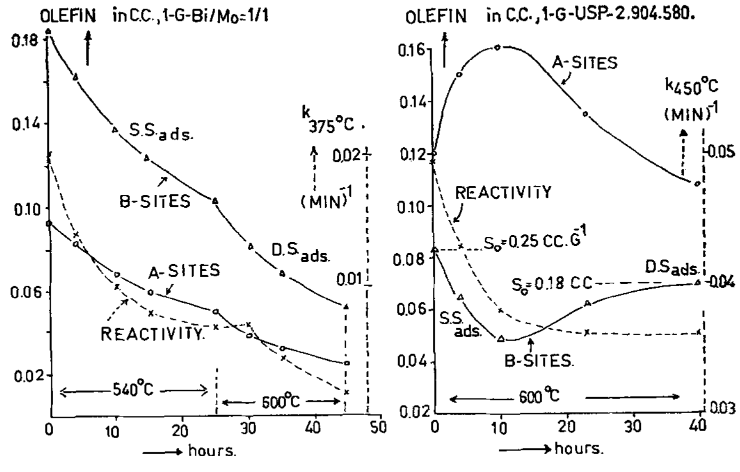

FIG. 3. (left) Adsorption properties of $Bi_2Mo_2O_9$ as a function of heating time. (right) Adsorption properties of SiO_2–$Bi_9PMo_{12}O_{52}$ as a function of heating time.

number of weak single-site adsorptions of butene on $Bi_2Mo_2O_9$ together with the decrease of the number of strong adsorption sites of butadiene during prolonged heating of catalyst. By analogy with the weak butene and the strong butadiene adsorption on koechlinite we shall call them B- and A-sites, respectively. It is also shown in Fig. 3 that during heating at 600°C the single-site adsorption of butene changes into a dual-site adsorption. Together with the observation that the color of the sample changes from white to yellow (the koechlinite color), this indicates that the Erman phase decomposes with formation of koechlinite and $Bi_2O_3 \cdot 3MoO_3$. However, the newly formed koechlinite phase must be a sintered one [see Matsuura and Schuit (*5*)] in agreement with the strong decrease in reactivity also shown in Fig. 3 by the broken line. Figure 3 (right) shows a similar behavior for the silica-supported Bi–Mo catalyst. Again the single-site type of weak butene adsorption decreases and changes into a dual-site adsorption characteristic for koechlinite. An interesting effect shown in Fig. 3 is the increase of the number of A-sites during the first 20 hr of heating of this catalyst at 600°C. Perhaps this effect is connected with further dehydroxylation of OH-groups; however, so far this increase has been left unexplained.

The decrease of the number of A-sites during prolonged heating is probably due to sintering of the koechlinite phase, the reactivity continuously going down. Comparison, however, of the two different catalysts in Fig. 3 shows the supported catalyst to be more stable than the nonsupported catalyst, the final reactivity ($k_{450} = 0.036$) being higher than that of the decomposed 1/1 phase with $k_{450} = 0.005$ which we calculated from $k_{375} = 0.002$.

That the butene adsorptions on these sintered catalysts are indeed dual-site adsorptions is shown in Fig. 4. Weak and single-site types of adsorption of butene and butadiene on $Bi_2O_3 \cdot 3MoO_3$ are represented in Fig. 5. It is shown here that the total volume of adsorption is low (0.02 $cm^3\ g^{-1}$). Furthermore, it turned out that it was impossible to detect a strong adsorption of butadiene.

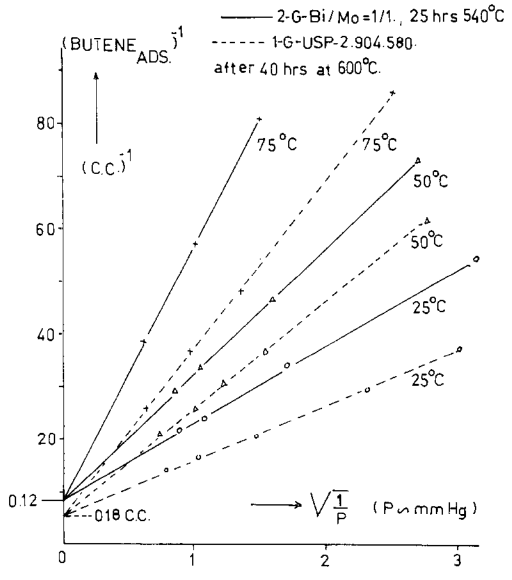

FIG. 4. Dual-site adsorptions of 1-butene on decomposed and sintered $Bi_2Mo_2O_9$ and SiO_2–$Bi_9PMo_{12}O_{52}$.

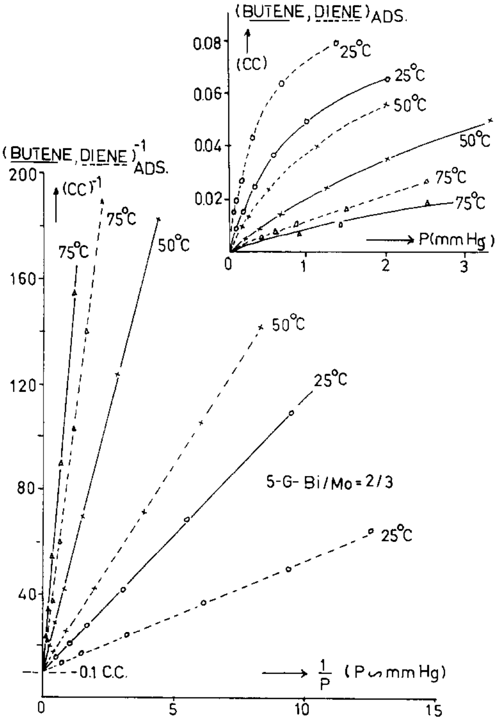

FIG. 5. Weak single-site type of adsorptions of 1-butene and butadiene on pure $Bi_2O_3 \cdot 3MoO_3$.

B. X-Ray Measurements

In Table 1 X-ray data are given for the $Bi_9PMo_{12}O_{52}$ catalyst prepared from phosphomolybdic acid. Although we observed appreciable line broadenings, the only compound observed is $Bi_2O_3{\cdot}3MoO_3$; not even traces of a possible new compound such as bismuth phosphomolybdate or $BiPO_4$ can be found. Further represented in Table 1 are the X-ray data of the silica-supported $Bi_9PMo_{12}O_{52}$ catalyst calcined at 560°C ("fresh catalyst"). It is obvious that the major component in the catalyst is the Erman phase, although some koechlinite lines ($d = 3.15$) are also observed. The characteristic 3.06 line of $Bi_2O_3{\cdot}3MoO_3$ is not present, which is surprising since the chemical composition of the catalyst is not far from the Bi/Mo ratio of 2/3.

TABLE 1

X-RAY DATA OF $Bi_9PMo_{12}O_{52}$ AND OF SILICA-SUPPORTED $Bi_9PMo_{12}O_{52}$ CATALYST

$Bi_9PMo_{12}O_{52}$[a]		Fresh catalyst, 560°C[b,c]			Spent catalyst, after 1 yr ammoxidation		
d(Å)	I	d(Å)	I	Assignment[d]	d(Å)	I	Assignment
7.84	4	3.195	79	1/1	6.96	15	2/3
6.94	11	3.15	90	2/1	4.90	21	2/3
6.25	4	2.930	20	1/1	3.276	23	2/3
5.94	2	2.81	25	1/1	3.19	95	1/1 + 2/3?
5.39	4	2.64	22	2/3	3.15	125	2/1
5.08	3	1.954	32	1/1	3.06	53	2/3
4.88	17	1.865	14	2/3	2.90	28	
4.55	7	1.730	15	2/1	2.77	20	2/1
3.59	8	1.689	15	1/1	2.697	15	1/1
3.54	6	1.64	10	1/1	2.642	25	2/3
3.51	5	1.601	22	1/1	2.493	15	2/1
3.43	6				1.954	33	1/1
3.33	5	Fresh catalyst, 20 hr 600°C			1.924	15	2/1
3.255	10	4.90	15	2/3	1.866	15	2/3
3.185	66	3.57	16	2/3	1.730	15	2/1
3.055	42	3.54	16	1/1	1.720	20	2/3
2.884	17	3.20	50	1/1 + (2/3)?	1.697	15	2/3
2.77	9	3.15	150	2/1	1.657	12	2/1
2.489	9	3.06	22	2/3	1.635	10	1/1
2.25	6	2.93	25	1/1	1.604	20	1/1
2.125	4	2.64	31	2/3			
2.000	8	1.955	35	1/1			
1.995	7	1.866	23	2/3			
1.947	5	1.730	18	2/1			
1.939	5	1.720	15	2/3			
1.905	7	1.604	31	1/1			
1.882	9						
1.802	4						
1.763	4						
1.717	5						
1.694	6						
1.594	5						
1.558	4						

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[a] Prepared from phosphomolybdic acid.

[b] Prepared from ammonium heptamolybdate.

[c] The pure Erman phase prepared by Van den Elzen (*9*) did not show *d*-values 3.06 and 3.15 characteristic of $Bi_2O_3{\cdot}3MoO_3$ and $Bi_2O_3{\cdot}MoO_3$, resp.

[d] 2/1 = $Bi_2O_3{\cdot}1MoO_3$; 1/1 = $Bi_2O_3{\cdot}2MoO_3$; 2/3 = $Bi_2O_3{\cdot}3MoO_3$.

Not represented in Table 1 are the X-ray data of the fresh catalyst subsequently heated at 500°C in air for 50 hr, because the X-ray diagram remained unchanged. In contrast with the nonsupported Erman compound, which is unstable at this heating temperature (*6*, *8*), the silica-supported catalyst is stable. Possibly this is due to the heating temperature of 500°C which is 60°C lower than the calcination temperature 560°C of the fresh catalyst. The behavior of the fresh catalyst on further heating at 600°C for 20 hr is also shown in Table 1. The Erman phase for an important part is now found to be decomposed into the Bi/Mo = 2/3 and 2/1 compounds, the characteristic *d*-value 3.06 of $Bi_2O_3 \cdot 3MoO_3$ being now present, while the intensity of the 3.15 line belonging to koechlinite has increased. Thus the silica-supported $Bi_9PMo_{12}O_{52}$ catalyst is not stable at 600°C.

X-Ray data of samples after 26 hr and after 50 hr of producing butadiene have shown that after 26 hr of olefin oxidation at 470°C the characteristic 3.06 value of $Bi_2O_3 \cdot 3MoO_3$ was present, together with some other *d*-values of this phase. After 50 hr reaction the intensity of the 3.06 line became almost equal to that of the spent ammoxidation catalyst, the X-ray data of this sample being also represented in Table 1. The number of lines observed with the spent catalyst was greater and they were also sharper than those of the 26 and 50 hr samples, indicating an improved crystallization of the Bi/Mo phases during 1 yr of ammoxidation.

It is noteworthy that a thermal treatment of the supported catalyst at 500°C did not lead to changes in the X-ray pattern; reduction–reoxidation cycles at 470°C therefore appear to increase the rate of structural rearrangements. Comparison of the 26 and 50 hr samples with the fresh catalyst (Table 1) have shown a partial decomposition of the Erman phase, because we observed formation of the 3.06 reflection of the 2/3 phase and further an increase of the 3.15 reflection of the 2/3 phase. The 2/3- and 2/1-phases newly formed at 470°C are not sintered because reactivity remained unaltered.

Somewhat surprisingly the 3.20 reflection of the 1/1 phase does not seem to diminish in intensity. This can probably be attributed to the silica effect of line broadening which prevents identification of the strongest line 3.185 of the 2/3 phase which is very close to 3.20.

Decomposition of the Erman phase should lead to a decrease in intensity of the 3.20 line; simultaneous formation of the 2/3 phase, however, should have had the effect of increasing the 3.185 line intensity, the final result of line broadening leading to hardly any change. For characterization of the 2/3 phase, therefore, we remain strongly dependent on the appearence of the 3.06 line (the second strong one).

DISCUSSION

Both catalysts, $Bi_2Mo_2O_9$ and supported $Bi_9PMo_{12}O_{52}$, show two types of adsorption, a slow and strong type for butadiene and a fast and weak type for butadiene and 1-butene. They are, however, not completely identical with the adsorptions ascribed to A- and B-sites on the Bi_2MoO_6 catalyst (koechlinite). The slow and strong adsorption on both catalysts certainly is stronger than on koechlinite, and the weak adsorptions are single-site instead of dual-site. We believe, nevertheless, that although not identical, they are essentially similar. As for the weakly adsorbing sites (B-sites) we observed a transformation from single-site to dual-site adsorption for both catalysts when heated at 600°C for longer time, the X-ray data confirming the Erman phase to be unstable at this temperature. The results of adsorption measurements and those of X-ray studies therefore appear in agreement. However, there are differences observed as to the heating time, decomposition of the Erman phase being distinguished sooner by X-ray measurements than by measurements of adsorption properties. We therefore believe that the process of structural rearrangement starts in the bulk. Finally, it is obvious now that the supported catalyst is far more thermally stable than the $Bi_2Mo_2O_9$ catalyst.

X-Ray results on supported $Bi_9PMo_{12}O_{52}$ which had been exposed to reaction conditions at 470°C during 1 day, shows partial decomposition of the Erman phase. After 1 day of butadiene production the silica-supported Bi–P–Mo catalyst reacts in a state where all three bismuth molybdates are present. One might expect a similar result after 1 day of acrylonitrile production. Contrary to the suggestion that decomposition of the Erman phase always should lead to catalyst deactivation, we observed the decomposition at 470°C after 1 day of butadiene production to have no influence on catalyst activity. Thus the newly formed and supported Bi/Mo = 2/3 and 2/1 compounds, either as such or in combination, are active catalysts. Catalyst deactivation after 1 yr of ammoxidation of propene at 470°C might be caused by a very slow sintering process of all 3 types of bismuth molybdate crystals to bigger units.

Let us now turn to the presence of phosphorus in the supported catalyst. We did not succeed in preparing bismuth phosphomolybdates of compositions such as: $(Bi^{3+})\cdot(PMo_{12}O_{40})^{3-}$ and $(BiO)_3^{+}\cdot(PMo_{12}O_{40})^{3-}$. The result of reaction of phosphomolybdic acid with bismuth nitrate is not formation of a stable ternary compound but formation of the binary compound $Bi_2O_3\cdot 3MoO_3$, possibly contaminated with $BiPO_4$. Because of our negative result to arrive at bismuth phosphomolybdate as catalyst for olefin oxidation we have to look for other possibilities to explain the role of phosphorus. In our previous reports (*6*, *3*) concerned with Bi-molybdate preparations, we observed mass swelling in water at the Bi/Mo ratios of 2/3 and 1/1, sticky slurries with gelatinous properties being obtained. In another study (*11*) concerned with promoter actions, we observed that mass swelling did not occur if PO_4^{3-} ions were present during preparation of promoted catalyst. The PO_4^{3-} ion is known from colloid chemistry as a strong flocculation and antipeptization agent. This might indicate that its function is to prevent formation of gelatinous slurries.

Finally, we want to remark on some details which are of significance during preparation of active 1/1 catalysts. We do not recommend using phosphomolybdic acid instead of ammonium heptamolybdate, since we were never successful in obtaining an active catalyst on the basis of $P_2O_5\cdot 24MoO_3\cdot 30H_2O$ as the reagent for coprecipitation. This is probably due to a stimulated formation of the less active Bi_2O_3. $3MoO_3$ compound. Another difficulty is that with phosphomolybdic acid one is not able any more to use ammonia to maintain coprecipitation at a suitable pH, because the insoluble ammonium phosphomolybdate will be formed. We suggest that the fact that the Erman phase is predominantly formed when ammonium heptamolybdate is used [see also (*6*)] is connected with decomposition of the complex heptamolybdate ion. The explanation of such phenomena is obviously connected with the little studied problem of conversion of polymolybdate complexes to solid systems. Lack of relevant data in the literature makes it difficult to formulate a reliable model of the inorganic reactions occurring.

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