JOURNAL OF CATALYSIS 15, 101-105 (1969)

Preparation of Bismuth–Molybdenum Catalysts

JANUSZ BEREŚ, ALEKSANDER JANIK, AND JERZY WASILEWSKI

Institute of Heavy Organic Synthesis, Blachownia Śląska, Poland

Received September 10, 1968

The influence of the precipitation condition on phase composition of catalysts and their catalytic activity was investigated. The phase composition of catalysts, having the following empirical formula: $Bi_{12}Mo_{12}PO_x$, depends on the pH value, at which the system is subjected to evaporation or filtration. In the case of a strongly acid medium, at a $pH < 1$, the γ-phase and that of free MoO_3 are the main components of the catalyst. In the pH range from 1 to 5 also insignificant quantities of the α-phase are present besides the β-phase.

To form the β-phase (free from the α- and γ-phases) in an acid medium, it is necessary to increase the Bi/Mo ratio above 1. This can be achieved, by increasing slightly the Bi content or binding a part of Mo as magnesium molybdate.

The catalysts containing the β-phase alone, are characterized by a high activity in the process of acrylonitrile synthesis, and enable to obtain a propylene conversion above 90% at a temp. 490°C, the selectivity being about 80%.

INTRODUCTION

So far, a good deal of work has already been devoted to investigations on bismuth–molybdenum catalysts used for the reaction of allylic oxidation of olefins. According to most of the reports on these investigations, the highest catalytic activity is achieved when the atomic ratio of Bi to Mo equals 1 (*1, 2*).

Many data (*3–5*) indicate that the presence of a new compound, $Bi_2O_3 \times 2MoO_3$, the so called β-phase, corresponds to this composition.

The different preparation methods, consisting in sintering or fusion of finely powdered oxides (*4–6*), precipitation or the use of solutions of bismuth or molybdenum salts in nitric acid (*7, 8*), suggests that this has no essential effect on the physical and catalytic properties of the final product. Differences in the specific surface of samples, obtained as a result of fusing the oxides and by precipitation from solutions (*4*), have only been found.

But, the divergences appearing in various publications and relative to both the optimum composition (*7, 9*) and the mere existence of the β-phase (*5, 6, 12*), induced us to examine in more detail the preparation conditions of the discussed catalysts.

EXPERIMENTAL

The investigated catalysts have been prepared by mixing the corresponding quantities of solutions of bismuth nitrate and ammonium molybdate at a temperature of 20°C. The required pH value was obtained using a 5% ammonia solution. After filtration or evaporation of water, the product was dried at 120°C and calcined at 400°C during 16 hr.

The bismuth content of the investigated catalysts has been determined by EDTA titration, the molybdenum colorimetrically as Mo^V EDTA complex and the sulphur content gravimetrically.

In connection with the measuring technique adopted by us, the comparison of catalytic activity of the selected samples has been carried out using pelleted catalysts containing 70% of α-Al_2O_3. They have been prepared in a similar way, introducing the reactants to an aqueous suspension of a finely powdered carrier.

The comparison of catalytic activity of the selected catalysts, used for the ammoxidation of propylene, was carried out in a flow apparatus described earlier (*10*). The reaction was conducted at a temperature of 490°C, with a throughput of 2 moles C_3H_6/liter of catalyst/hour, the molar ratio of the reagents being $C_3H_6:NH_3:O_2:H_2O = 1:1:1.8:6$. The reactor having a diameter of 25 mm was each time charged with 215 cm^3 of the investigated catalyst in the form of pellets with a diameter of 5 mm and a height of 3 mm. The reaction products have been identified chromatographically.

The infra-red spectra have been performed using the spectrophotometer Unicam SP 200, the investigated samples were prepared in form of nujol suspensions.

The X-ray patterns of the catalyst powders with or without Al_2O_3 have been obtained using an apparatus of the type TUR 60. CuKα radiation and Debye-Scherrer type cameras of 57-mm diameter were used. According to Kolchin *et al.* (*4*) we have adopted the symbols:

"α"—to designate the phase $Bi_2O_3 \cdot 3MoO_3$,
"β"—to designate the phase $Bi_2O_3 \cdot 2MoO_3$,
"γ"—to designate the phase $Bi_2O_3 \cdot MoO_3$.

RESULTS AND DISCUSSION

The catalysts obtained using various starting solutions are shown in Table 1.

The meaning of the symbols used in the tables given below is as follows:

"F"—catalysts dried after filtration;
"E"—catalysts dried after evaporation;
"s"—catalysts precipitated at a constant pH,
"a"—pH adjusted to a definite value after precipitation;

Samples 1–3 were obtained by using a 15% HNO_3^-; Sample 4 by using a 1 *N* HNO_3^- solution.

Sample 5 was obtained without addition of acid. The remaining catalysts, shown in Table 1 were prepared by adding dropwise an aqueous solution of ammonium molybdate and H_3PO_4 and, simultaneously a solution of bismuth nitrate in 1 *N* HNO_3.

The experimental results show a considerable influence of the preparation method on the phase composition of the catalyst. In spite of the use of reagents in stoichiometric quantities, corresponding to the composition of the β-phase, the main components of the products obtained in the strongly acid solutions are the γ-phase and free MoO_3. This fact is undoubtedly associated with the presence of polyacids in the range of low pH values, and with the formation of cationic forms of molybdenum below pH = 0.5 (*11*). It can be assumed that for the formation of the compound $Bi_2O_3 \times 2MoO_3$, the presence of a monomeric form of molybdenum acid is necessary. This can be achieved e.g. through a reaction carried out for 2 hr at pH = 7.

Subjecting the samples of catalyst to drying and subsequently to calcination, immediately after neutralization or without neutralization, leads to a decomposition of polymolybdenum acid to free MoO_3, which, under conditions adopted by us, undergoes only partially a further reaction with bismuth giving small quantities of β-phase and a compound with a low molybdenum content, i.e. $Bi_2O_3 \cdot MoO_3$.

The diffraction lines of the β-phase in the catalyst No. 2, subjected to evaporation immediately after neutralization, are considerably more intense in comparison with those of the catalyst No. 1, obtained without neutralization (Figs. 1 and 2). However, only the reaction carried out for 2 hr at a pH value of 7 leads to a complete disappearance of the lines of the γ-phase and those of free MoO_3. (Fig. 3).

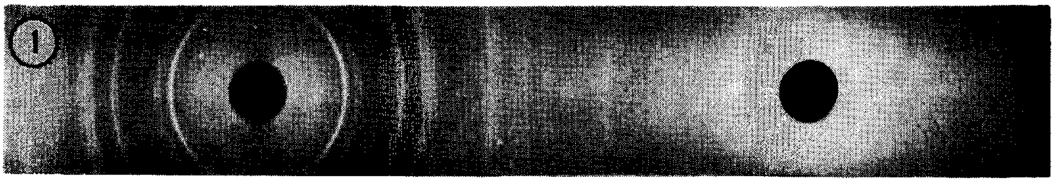
It must here be underlined that it is not always easy to determine unequivocally the phase composition of the investigated catalysts, and it is very often necessary to confront the data obtained by X-ray analysis with those obtained by infra-red spectrophotometry. It concerns in particular the ascertainment of the presence or absence of free MoO_3.

The occurrence of a band at about 980 cm^{-1}, which disappears after treating the sample with an ammonia solution, has been adopted as a criterion for the presence of free MoO_3 (Fig. 4).

The β-phase constitutes the main phase in catalysts prepared using 1 *N* HNO_3 and subjected to neutralization. Also, the catalysts prepared without use of HNO_3 do

TABLE 1
INFLUENCE OF THE PREPARATION METHOD ON THE PHASE COMPOSITION OF THE CATALYST HAVING THE EMPIRICAL FORMULA: $Bi_{12}Mo_{12}PO_x$

No. of catalyst	Starting solutions	Preparation method	Phase composition
1 (E)		Evaporation	$\gamma + MoO_3 + \beta$
2 (aE)	$Bi(NO_3)_3 \cdot 5H_2O$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in a 15% HNO_3	Neutralization using a 5% NH_4OH and evaporation	$\gamma + \beta + MoO_3$
3 (aE)		As above; mixing during 2 hr after neutralization	$\beta + \alpha$(Traces)
4 (E)	$Bi(NO_3)_3 \cdot 5H_2O$ in 1 N HNO_3 $(NH_4)_6Mo_7O_{24} \cdot 4H_2O + H_3PO_4$ in H_2O	Dropping ammonium molybdate into the solution of bismuth nitrate and evaporation	$\gamma + MoO_3 + \beta$
5 (aE)	Suspension of basic bismuth nitrate in H_2O, and an aqueous solution of ammonium molybdate	Solution of Mo dropped into the suspension of Bi salts and neutralization with ammonia	$\beta + \alpha$(low content)
6 (aF)	$Bi(NO_3)_3 \cdot 5H_2O$ in 1N HNO_3 and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and H_3PO_4 in water:	Simultaneous dropping of solutions, bringing the pH up to 3 filtration and neutralization of precipitate with ammonia	$\beta + \alpha$(Traces)
7 (sE)	As above	Simultaneous feeding of the two solutions and ammonia at a pH = 7; and evaporation	β
8 (aE)	As above	Simultaneous feeding of solutions and then neutralization and evaporation	β



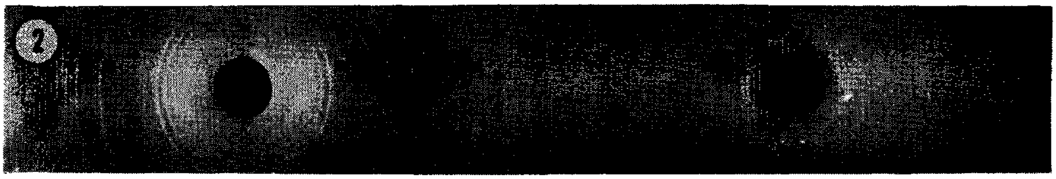


FIG. 1. X-Rays Debyegramme for catalyst nr 1E.
FIG. 2. X-Rays Debyegramme for catalyst nr 2 aE.
FIG. 3. X-Rays Debyegramme for catalyst nr 3 aE.

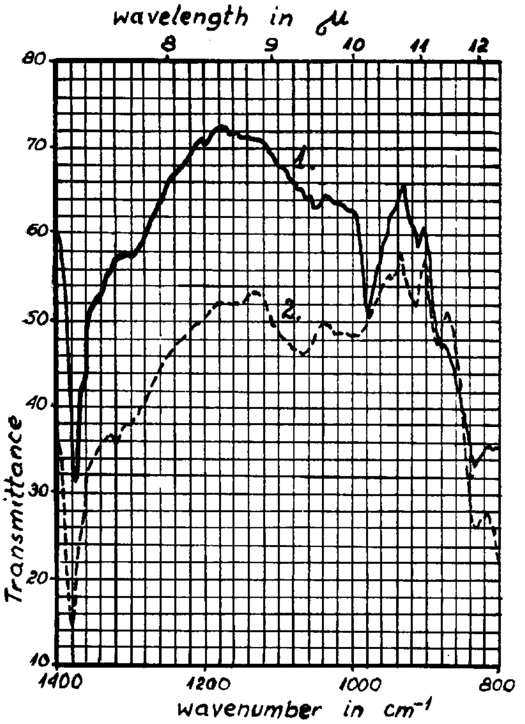


FIG. 4. Spectrum of catalyst nr 4: 1—before treatment with ammonia water; 2—after treatment with ammonia water.

not show lines of the γ-phase and those of MoO_3. (Samples 5, 7, and 8.)

The above observations induced us to carry out, in the subsequent part of our work, more detailed investigations on the influence of the pH. In these experiments we used only an aqueous solution of ammonium molybdate and H_3PO_4, as well as, a 1 *N* HNO_3 solution of bismuth nitrate. These compounds were simultaneously fed to the reaction medium, this operation being accompanied by an active agitation.

In the case of catalysts containing 70% of Al_3O_3, the above-mentioned solutions were simultaneously fed into the aqueous suspension of finely powdered carrier. The required pH values were obtained by feeding a corresponding quantity of a 5% ammonia solution immediately after the mixing of solutions of bismuth and molybdenum salts.

Some of the investigated catalysts were prepared with simultaneous addition of ammonia. This assured the maintenance of a constant pH value during precipitation (catalysts designated by the symbol "s"). The experimental results of these series of investigations, together with those obtained from the ammoxidation tests of propylene, carried out in presence of these catalysts are summarized in Table 2.

It results from the above compilation that in the case of catalysts having the empirical formula: $Bi_{12}Mo_{12}PO_x$, when obtained in an acid medium, a small quantity of the α-phase is present besides the β-phase. The intensity of lines of the α-phase decreases with increasing pH, and they are not found at a $pH = 7$.

The figures obtained for acrylonitrile synthesis with catalysts prepared within the range of investigated pH values, are very similar, which indicates that the insignificant content of other phases in the β-phase has no considerable effect on the ammoxidation process.

The highest conversion of propylene, with simultaneous high selectivity in relation to acrylonitrile, has been obtained in a pH range from 5 to 7.

To prevent the formation of the α-phase having a higher molybdenum content than the β-phase, the subsequent catalysts were made with a higher atomic ratio of Bi/Mo.

According to our presumption, this has led to a disappearance of the α-phase, even in the case of samples prepared in an acid medium ($pH = 2$ and 3).

This effect has been obtained as well by increasing the Bi content to a quantity corresponding to the formulas $Bi_{13}Mo_{12}PO_x$ and $Bi_{14}Mo_{12}PO_x$ as by replacing a part of bismuth with magnesium, which binds the excess of molybdenum in form of the compound $MgO \cdot MoO_3$.

All systems discussed above show a high activity for the acrylonitrile synthesis. This makes it possible to obtain a conversion of propylene above 90%.

A higher magnesium content (the catalyst $Bi_6Mg_9Mo_{12}PO_x$) leads just to the formation of the γ-phase. In the latter case, a decrease of propylene conversion by about 20% takes place.

TABLE 2
INFLUENCE OF pH ON THE PROPERTIES OF CATALYSTS

No. of catalyst	Total formula	Precipitation pH	Phase composition	Specific Surface of Catalyst		Conversion of propylene (%)	Selectivity to acrylonitrile (%)
				Without carrier (m^2/g)	With carrier (m^2/g)		
1 a-F		1	$\beta + \alpha$ Traces	1.92	0.90	84.2	83.5
2 a-F		2	$\beta + \alpha$ Traces	1.99	0.82	88.5	77.7
3 a-F	$Bi_{12}Mo_{12}PO_x$	2	$\beta + \alpha$ Traces	3.08	—	86.5	82.2
4 a-F		3	$\beta + \alpha$ Traces	1.82	0.78	83.8	83.5
5 a-F		5	$\beta + \alpha$ Traces	2.10	1.00	88.7	83.5
6 a-E		7	β	5.40	1.67	89.3	80.0
7 a-F		2	β	2.27	1.24	93.7	78.6
8 s-F		3	β	3.70	—	—	—
9 a-F	$Bi_{13}Mo_{12}PO_x$	3	β	3.00	—	—	—
10 a-F		5	β	—	—	91.7	79.7
11 a-F		7[a]	β	4.10	—	90.8	80.1
12 a-F		2	β	3.50	1.28	87.0	84.0
13 s-F	$Bi_{14}Mo_{12}PO_x$	2	β	4.20	—	—	—
14 a-F		7	β	5.90	1.69	92.3	82.4
15 a-E	$Bi_{10}Mg_3Mo_{12}PO_x$	7	$\beta + MgO{\cdot}MoO_3$	3.50	—	87.3	78.3
16 a-F	$Bi_{10,6}Mg_3PO_xMo_{12}$	7[a]	$\beta + MgO{\cdot}MoO_3$	—	—	91.5	75.6
17 a-E	$Bi_6Mg_9Mo_{12}PO_x$	7	$\gamma + MgO{\cdot}MoO_3$	4.80	—	73.4	75.1

[a] Catalyst filtrated at pH = 3 and neutralized with ammonia.

REFERENCES

1. Adams, C. R., *Proc. Third Intern. Congress on Catalysis, Amsterdam, 1964.*
2. Stroeva, S. S., Gel'bshtein, A. J., Kul'kova, N. V., Shcheglova, G. G., Ezhkova, Z. J., and Roginskaya, Yu. E., *Neftekhimiya* **6,** 412 (1966).
3. Gel'bshtein, A. I., Stroeva, S. S., Kul'kova, N. V., Bakshi, Yu. M., Lapidus, V. L., Vasil'eva, I. B., and Sevast'yanov, N. G., *Neftekhimiya* **4,** 908 (1964).
4. Kolchin, I. K., Bobkov, S. S., and Margolis, L. Ya., *Neftekhimiya* **4,** 301 (1964).
5. Erman, L. J., Galperin, E. L., Kolchin, I. K., Dobrzhanskiĭ, G. F., and Chernyshev, K. S., *Zh. Neorg. Khim.* **9,** 2174 (1964).
6. Bleijenberg, A. C., Lippens, B. C., and Schuit, G. C. A., *J. Catalysis* **4,** 581 (1965).
7. Sachtler, W. M., and de Boer, N. H., *Proc. Third Intern. Congress on Catalysis, Amsterdam, 1964.*
8. Kolobikhin, V. A., and Emel'yanova, R. N., *Neftekhimiya* **4,** 829 (1964).
9. Belenkii, M. S., Alkhazov, T. G., Bartanov, A. A., and Alabekova, O. A., *Neft. Gaz* **8,** 48 (1964).
10. Wasilewski, J., Bereš, J., and Perkowski, J., *Brennstoff Chem.* **49,** 120 (1968).
11. Babko, A. K., and Gridchina, G. I., *Zh. Neorg. Khim.* **13,** 123 (1968).
12. Janik, A., *Roczniki Chem.* **41,** 1399 (1967). Janik, A., *Roczniki Chem.* (In press.)