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On the Preparation of Bismuth Molybdate Koechlinite Catalyst

Recently (*1*) a slurry reaction between 0.2 mol $BiONO_3$ and 0.1 mol H_2MoO_4 in 1 liter of boiling water was recommended in this Journal for preparation of a Bi_2MoO_6 catalyst that after calcination at 500°C was very active and selective for olefin oxidations: The crystal phase of the catalyst showed similarities with the mineral koechlinite.

Since this method was rather unusual and not completely understood, more details are now given of the earlier published preparations (exp. nos. 5, 6, 7) in order to ensure that anyone interested can prepare his own active Bi_2MoO_6 catalyst. A further aim of this Note is to connect the preparational aspects with the problems of activity and selectivity.

An important factor in the slurry reactions is the quality of the molybdic acid used. Trademark molybdic acid usually contains appreciable amounts of acid ammonium molybdate $(NH_4)\cdot HMoO_4$, which is very soluble in boiling water, easily leading to undesired slurry reactions. For instance, BDH molybdic acid analyzed according to the Kjeldahl method for the ammonia content showed the presence of 5.5 wt% NH_3. This means that this material is a mixture of about 50 wt% H_2MoO_4 and 50 wt% $(NH_4)\cdot HMoO_4$. A simple solubility experiment in 1 liter of boiling water showed that from 16.2 g of BDH molybdic acid an amount of 13 g was dissolved. A similar experiment, after neutralizing the 5.5% NH_3 with HNO_3, showed that from 16.2 g of molybdic acid now only an amount of 1 g was dissolved.

To obtain a reliable procedure for preparation of an active Bi_2MoO_6 catalyst, we have studied the influence of the solubility of BDH molybdic acid on the slurry reaction desired:

$$2\ BiONO_3 + H_2MoO_4 \rightarrow (BiO)_2MoO_4 + 2\ HNO_3.$$

To give the highest assurance for the exact Bi/Mo ratio of 2/1 in our samples we have worked quantitatively: We analyzed raw materials, calculated and checked the expected weight of catalyst, and finally analyzed the water filtrates and filter papers. In all preparations we started with 16.1767 g of BDH molybdic acid containing 88.98 wt% MoO_3 and with 58.2887 g of Merck bismuthyl nitrate containing 79.94 wt% Bi_2O_3. With Kjeldahl analysis, no NH_3 was found to be present in this bismuthyl nitrate. From these amounts a final weight of 60.990 g of Bi_2MoO_6 is to be expected. For stirring we used a propeller with a length of 5 cm, and the velocity of stirring was 1200 rotations per minute.

Method A. In this preparation the solubility of molybdic acid was increased by adding 138.7 mmol of ammonia. All molybdic acid dissolved in 1 liter of hot water, after which we started the reaction by adding insoluble bismuthyl nitrate. After 1 hr of stirring and boiling we observed swelling of the white mass, an effect earlier (*1*) observed to be characteristic of the formation of the $Bi_2(MoO_4)_3$-phase. Only after 6 hr of slurry reaction did the color very slowly change from white to yellow. After 18 hr of reaction the mass, filtered, dried, and calcined at 500°C, showed a weight of 60.68 g. The missing amount, of the order of 300 mg, was discovered for the most part in the filter

TABLE 1

Butene Oxidation Test Results for 400 mg of Catalysts Obtained by Method B and by Improved Variants of Method B[a]

Method B

T (°C)	340	360	380	400	420	440
CO_2	0.7	13.0	13.3	12.9	12.9	12.8
$C_4^{2-} - 1$	96.9	31.5	19.3	19.3	20.0	16.9
Isomers	1.4	1.1	1.9	1.8	—	—
C_4^{4-}	1.0	54.4	65.5	66.0	67.1	70.3
Act.	1.7	67.3	78.8	78.9	79.9	83.1
Select.	58.9	80.7	83.2	83.6	83.9	84.6

First improved Method B: $Bi_2Mo_{1.02}\cdot O_6$ (nonstoichiometric)

T (°C)	340	360	380	400	420	440
CO_2	0.8	1.1	2.0	3.2	3.7	4.3
$C_4^{2-} - 1$	87.2	84.9	69.9	40.0	3.4	1.4
Isomers	3.2	2.6	4.4	6.4	6.1	5.4
C_4^{4-}	8.7	11.4	23.8	50.5	86.8	88.9
Act.	9.6	12.5	25.8	53.7	90.5	93.2
Select.	91.4	91.3	92.4	94.0	95.9	95.4

Second improved Method B: Bi_2MoO_6 (stoichiometric)

T (°C)	340	360	380	400	420	440	460
Act.	6.3	9.8	11.4	29.0	67.9	79.8	82.4
Select.	96.4	92.4	92.3	94.3	96.5	94.6	94.5

Note. For all catalysts, during preparation, the addition of a small amount of ammonia at the end of slurry reactions is omitted. Slurry reaction time was 12 hr.

[a] Flows of 15 cm^3 min^{-1} 1-butene and 105 cm^3 min^{-1} artificial air (80% He + 20% O_2); activity = $(C_4^{4-} + CO_2)/100$, selectivity = $C_4^{4-}/(C_4^{4-} + CO_2)$.

papers, which were burned to ash. By evaporating the water filtrate we obtained a mixture of ammonium nitrate and HNO_3 that after heating at 300 and 500°C showed a mass residue of the order of 20 mg. A slightly yellow-colored catalyst with a surface area of 10.7 m^2 g^{-1} was obtained showing *no activity* at all for the 1-butene oxidation.

Method B. In this experiment the solubility of the 5.5% ammonia containing molybdic acid was suppressed by adding 50 mmol of HNO_3 which transformed the $(NH_4)\cdot HMoO_4$ into NH_4NO_3 and H_2MoO_4. Now starting the slurry reaction with bismuthyl nitrate, within 2 hr we observed the color change from white to yellow without any swelling effects. After 10 hr of reaction the yellow color was very intense, and to lower the acidity of the boiling water a little we added an amount of NH_3 equivalent to the 5.5%. Finally, after 12 hr of reaction the yellow-colored mass was filtered, dried, and calcined at 500°C, after which it showed a weight of 60.86 g. Again the missing amount, 130 mg, was discovered for the most part in the filter papers, and a small part, in a residue obtained after evaporation of the filtrate. A bright yellow-colored catalyst (surface area 7.9 m^2 g^{-1}) was obtained showing excellent activity for 1-butene oxidation. An equally active catalyst was obtained by a repetition of Method B in which the addition of a small amount of ammonia at the end of the slurry reaction was omitted, the test results of this catalyst being represented in Table 1.

Method C. In this preparation we used the raw materials as such without any addition of ammonia or nitric acid. Directly from the beginning of the slurry reaction a major part of the molybdic acid started to dissolve in hot water. However, the applied stirring was fast, so that the remaining slurry reaction between bismuthyl nitrate and the undissolved part of molybdic acid rather quickly produced HNO_3 which in its turn reprecipitated the dissolved part of the molybdic acid. After 18 hr of reaction and after filtration, drying, and calcination at 500°C, we obtained 60.79 g of light yellow-colored catalyst (surface area of 7.3 $m^2 g^{-1}$) which was moderately active for 1-butene oxidation. It turned out that the results obtained with Method C are strongly dependent on the stirring rate, since a very poorly active catalyst was obtained with 600 rotations per minute (mass swelling was observed).

With the above three examples, we have shown the significance of the problem of solubility of molybdic acid. It now appears very likely that for obtaining an active Bi_2MoO_6 catalyst, one must from the beginning create acid conditions in order to reduce strongly the solubility of molybdic acid, which assures a slurry reaction between two solid but wet substances in the correct ratio of 2/1.

The following observations with respect to the problem of the activity are very disappointing. (1) Infrared spectra of the three samples were similar, showing only small differences from which hardly any conclusions could be drawn. (2) The X-ray diagrams of the samples all show the koechlinite pattern. Sample A shows only vague indications that $Bi_2(MoO_4)_3$ is present: Sample B gives the highest intensities of koechlinite lines. (3) The Surface area of the inactive catalyst from Method A is higher than that of the active catalyst from Method B.

Before discussing the problem of the activity we will reconsider Method B, which gave the catalyst with a selectivity of 84%, which is not particularly high. It indicates the presence of nonselective sites. Two improvements in selectivity with catalyst from Method B will now be described, both based on similar considerations, the first leading to a nonstoichiometric and the second to a stoichiometric koechlinite phase.

In considering the slurry reaction we must realize that Method B is not ideal. Depending on the rotation speed of the stirrer, many collisions between the solid phase particles have to occur to build up the MoO_2 and Bi_2O_2 layers in the twinned way that is characteristic for the koechlinite structure. It is therefore conceivable that small errors easily arise; for instance, in a long series of Mo–O–Bi–O–Mo–O–Bi... elements, small Bi–O–Bi and Mo–O–Mo elements can intrude. It is suggested that the errors arising from Bi–O–Bi elements lead to nonselective or combustion sites at the surface of catalyst, since in comparing Bi_2O_3 with MoO_3 it is the first one which is completely nonselective. It is obvious now that a slight excess of molybdic acid should have a favorable effect in elimination of these nonselective sites. The best results with Method B were obtained by use of a slight excess of 2 wt% of molybdic acid (see Table 1). With an excess of 4%, a certain decline was observed.

Another consequence of the collisions between the $BiONO_3$ and H_2MoO_4 particles in Method B is that the larger the particles are, the easier will errors arise in the regularity of the alternating Bi_2O_2 and MoO_2 layers. Hence ball milling of the $BiONO_3$ and H_2MoO_4 powders before starting the slurry reaction must have a favorable effect on the final selectivity. Molybdic acid and bismuthyl nitrate, separated, were ball milled for 5 hr in agate mortars until very fine powders were obtained, after which Method B was applied with the one difference that in order to increase the number of collisions 0.5 liter of water instead of 1 liter was used. Now a stoichiometric Bi_2MoO_6 catalyst with surface area of 4.2 m^2 g^{-1} was obtained. The test results represented in Table 1 show that indeed a stoichiometric 2/1 catalyst can reach a selectivity of 95%, which confirms our suggestion that for obtaining high selectivity one has to eliminate the formation of nonselective sites. In addition, this experiment with ball-milled materials provides a strong argument that for preparing active and selective catalysts for oxidation of 1-butene we really must deal with inorganic reactions via solid but wet phases and not via dissolved phases, since in the latter case ball milling will have no effect at all. Another argument that points to solid phase reaction is that during the cooling down of the hot water we never observed crystallization of the material.

With respect to the problem of selectivity it is noteworthy to mention here that using Method B we have prepared a nonstoichiometric catalyst of the composition Bi/Mo = 2.02/1. This phase with a small excess of 1 wt% Bi in it was considerably lower in its activity, showing that now the major part of the selective sites was eliminated, the nonselective sites still being operative for combustion of 1-butene. The X-ray diagram of this sample showed a koechlinite pattern with considerable loss in intensities of lines.

It is necessary to discuss some consequences of a different nature:

(1) The catalysts described in Table 1 failed to produce the much discussed broad ESR signal, which was believed to be related to a Bi^{5+} formation.

(2) The Bi/Mo = 2/1.02 catalyst in its activity and selectivity pattern is comparable to the multicomponent molybdate catalysts which were described earlier (*2*) as being composed of particles possessing a Bi/Mo = 2/1 skin activated by Fe^{3+}. The concepts for the activation of (a) easier electron transfer and (b) $Bi^{3+} + 2\ Fe^{3+} \rightarrow Bi^{5+} + 2\ Fe^{2+}$, are no longer necessary if we assume that the skin is composed of a Bi/Mo material similar to that of our Bi/Mo = 2/1.02 catalyst.

(3) Vacuum treatments of our catalysts at 480°C and 10^{-6} mm Hg showed formation of Bi mirrors at the cold part of the glass tubes. Reoxidation of the remaining grey-colored Bi–Mo phase showed that as a result of this treatment the catalyst was sintered. There was (a) a loss of 50% in surface area, (b) further crystallization of particles, (c) a decrease of 20% in activity and (d) a decrease of 8% in selectivity.

Hence, vacuum treatments at elevated temperatures are not to be recommended in studies of the surface situation of the fresh catalyst. Strictly, these treatments are inadmissible, since for building up a consistent picture of the surface one has to take care that this surface remains in its original state. It is unfortunate that Matsuura (*3*), in his extensive adsorption studies, ignored the importance of the Bi mirrors formed during his vacuum preheatings.

We can now give a reasonable explanation why Method A gave inactive and why Method B gave active koechlinite catalysts. In the literature (*4*) the structure of molybdic acid is described as containing octahedral surroundings of Mo by oxygens, the octahedra being partly connected via corners and partly via edges. Since in the mineral koechlinte a similar surrounding for Mo is present, it appears that molybdic acid is the most suitable inorganic reagent for preparing koechlinite: All that is necessary is the insertion of Bi_2O_2 layers in a twinned way via collisions of particles, the formed and dissolved HNO_3 being the factor for facilitating this process, which is easy to follow by measuring the change in pH. It should be mentioned that the X-ray pattern of a dried sample already points to a nascent koechlinite phase.

Dissolved Mo (Method A) in the form of MoO_4^{2-} is known in the literature (*5*) to have tetrahedral surrounding by oxygens. The same type of Mo surrounding is present in the compound $Bi_2Mo_3O_{12}$, which was found to be inactive (*1*) provided it is prepared as pure as possible. These facts make it understandable that in Method A the mass swelling characteristic of the $\frac{2}{3}$-phase formation was observed. Directly from the beginning the desired solid phase reaction went wrong: The $\frac{2}{3}$-phase and consequently phases richer in Bi than 2/1 (also known to be inactive) are formed during reaction in boiling water. Obviously, these phases after drying and calcination (further reactions) are producing an inactive (pseudo) koechlinite phase, the distances between the metal ions being similar to those in normal koechlinite; however, differences in the oxygen positions are to be expected. It is conceivable that these differences are restricted to the surface. In the terminology of skins it is possible that a thin skin of $Bi_2Mo_3O_{12}$ is covering the koechlinite particles. A final answer on this problem can be given only when new physical techniques or instruments are developed which are able to give information on the oxygen positions.

Finally, we wish to remark that (a) activity per unit of surface area (from nitrogen adsorption) is a dangerous parameter for comparing different catalyst samples, in particular when preparational backgrounds are not fully understood; (b) the kinetics of koechlinite formation during slurry reaction now need to be studied. According to our description of the insertion of Bi_2O_2 layers in molybdic acid particles, one has to expect that diffusional processes are becoming operative.

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