From the present results we conclude that the catalytic activity of silver-on-silica is mainly if not entirely due to its capability of decomposing hydroperoxides into chain-initiating radicals.

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Koechlinite. An Active, Selective and Sensitive Acrylonitrile Catalyst

In a previous paper (*1*) we reported on the preparation of bismuth molybdates and in particular on the preparation of Bi_2MoO_6, koechlinite, which was a highly active and selective catalyst for 1-butene oxidation. The latter was obtained from a slurry reaction between basic bismuth nitrate (bismuthyl nitrate) and molybdic acid in boiling water. The inorganic synthesis was proved to proceed according the following equation:

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

During 20 hr stirring and boiling of the slurry, the pH was found to decrease from 7 to 2. After filtration, drying and calcination at 500°C a sample with an X-ray pattern was obtained similar to that of the mineral koechlinite. This catalyst (selective for 1-butene oxidation), which was discussed during a recent A.C.S. Meeting (Boston, April 9–14, 1972), was not very selective for ammoxidation of propene. The yield of acrylonitrile was found to be about 45% and in particular ammonia combustion was high on this catalyst. To explain this behavior we have to consider that recently Bi_2O_3 was reported as a catalyst for ammonia combustion (*2*). One possibility therefore is that our prepared koechlinite was not completely pure. It might have contained small amounts of Bi_2O_3, difficult to detect by X-ray measurements. We decided therefore to restudy our method of preparation with a view to improving it, and to examine two important aspects: (1) by eliminating the possibility that some Bi_2O_3 could be present to see whether this leads to a good acrylonitril catalyst, (2) the aspect of olefin adsorptions. The koechlinite phase prepared as described earlier (*1*) showed olefin adsorptions of the order of 0.12 $cm^3\ g^{-1}$ catalyst (*3*). This amount is lower than on a commercial Bi/Mo catalyst (US P 2.904.580) where silica as a carrier was used. Considering the 50% silica content, this number becomes 0.50 $cm^3\ g^{-1}$ Bi/Mo compounds. Since the carrier interferes in the characterization of the physical properties of the active component and creates uncertainty, we were interested in preparing a pure koechlinite phase with a comparable or even higher olefin adsorption. Such a material could then be valuable in solving the difficult problems in ESR and infrared adsorption measurements.

A. CATALYST PREPARATION AND CHARACTERIZATION

The same procedure was followed as reported earlier (*1*) under Expt. No. 6. However, after 20 hr of slurry reaction, the water with pH = 2 was removed by filtration of the yellow colored mass. Fresh water was then added and boiling and stirring of the slurry was started again. During 10 hr the pH changed from 7 to 3.5 and again the acid-containing water was replaced by fresh water. After 5 hr boiling and stirring the pH changed from 7 to 5.5. This procedure of refreshing the water was repeated until no change of the pH (=7) could be observed, indicating clearly that Reaction (1) was completely finished. Analysis of the water filtrates showed that neither Bi nor Mo compounds were present. The yellow substance in the wet form, containing a small amount of water, was further treated according to two different procedures: (1) it was dried and calcined for 2 hr at 500°C to obtain a catalyst for testing again the ammoxidation reaction; (2) the wet substance was several times (7×) brought into contact with an excess of liquid nitrogen and after each treatment (evaporation of nitrogen) was warmed to room temperature. The color of the mass changed from yellow to slightly green and the viscosity increased. Filtration, to remove water, proceeded very slowly. Then the material was dried at 110°C. The powder, now at a temperature of 250°C, was evacuated in the adsorption apparatus (*3*) at a pressure of 10^{-6} Torr in order to complete the dehydroxylation reaction. The water formed was condensed in a cold trap. During this process the color changed into gray-black. Obviously, during dehydroxylation also some oxygen was dissociated from the catalyst. After 3 hr dehydroxylation, oxygen was added at 300°C and quickly the color turned to yellow again. This material was ready for characterization.

1. The Sample Calcined at 500°C

The X-ray diagram showed all the characteristic lines of the mineral koechlinite. On this newly prepared sample, Matsuura discovered an E.S.R. signal completely different from that reported in the literature (*4*) and the new results will be published by him. The material calcined at 500°C was not suitable for making self-supporting pellets for infrared measurements.

2. The Nitrogen-treated Sample

(a) X-ray diagram: all peaks belonging to koechlinite were present at exactly the same *d*-values, but some of them showed appreciable line broadening, indicating the presence of small crystals; (b) Stereoscan photographs: comparison of the sample with the older sample (see Batist *et al.* (*1*)) showed the presence of smaller globules; (c) Dehydrogenation selectivity, tested as before (*1*): selectivity was not affected by this treatment, and activity was better; (d) Adsorption measurements: Matsuura has found weak olefin adsorption (B sites) with a volume of 3.4 $cm^3\ g^{-1}$, which is a factor of 30 higher than on the old sample. For strong butadiene adsorption (A sites) he found 0.82 $cm^3\ g^{-1}$, a factor 34 higher than on the old sample.

A crucial point of the liquid nitrogen treatment was that we obtained a material suitable for making self-supporting sample pellets for ir work which had fairly high transmissions in the hydrocarbon bending and stretching regions. The study of the adsorption of hydrocarbons using infrared spectroscopy is now in progress.

B. AMMOXIDATION OF PROPENE

According to the reaction:

$$C_3H_6 + NH_3 + 3/2O_2 \rightarrow C_3H_3N + 3H_2O \qquad (2)$$

the following experiment has been carried out. The reactor was filled with a mixture of 7 g koechlinite (particle size 1–2 mm) and 95 g carborundum (SiC) (particle size 1–1.4 mm). The following feed composition in mole % was used: C_3H_6 5.3, NH_3 4.3, O_2 8.7, H_2O 6.7, He 75.0. The feed rate was 300 $cm^3\ min^{-1}$, which gives a residence time of 2.8 sec. The contact time was 0.05 sec and the space velocity was 0.26 g C_3H_6 (g cat)$^{-1}$ hr^{-1}. Reaction temperature was 445°C.

Analysis was carried out with a heated

katharometer programmed chromatograph (Philips/Pye, Model 44). A complete analysis could be obtained by applying two column combinations in parallel operation. The first column was in glass (diameter 2 mm), containing 1 m Porapak Q and 1.3 m Porapak T (particle size 50–80 mesh). The gas flow rate was 30 cm^3 min^{-1}, with temperature programming from 60 to 180°C at 10°C min^{-1}. The analysis time was 20 min, with the following peaks recorded successively: ($O_2 + N_2 + CO$), CO_2, NH_3, C_3H_6, H_2O, C_2H_4O, C_3H_4O, C_2H_3N, C_3H_3N. The second column combination consisted of a precolumn filled with Porapak T and a 2-m stainless steel column containing molecular sieve 13 × (50–80 mesh). The gas flow rate was 30 cm^3 min^{-1} at a temperature of 20°C. The components O_2, N_2, and CO were successively recorded in 3 min.

Results for feed and product composition (Table 1) show some differences in byproduct composition between koechlinite and a commercial Bi/Mo catalyst (e.g., CH_3CN). From the values in Table 1 we may calculate the contribution of C_3H_6 and NH_3 to the formation of acrylonitrile:

	C_3H_6	NH_3
Conversion %	82.9	97.8
Selectivity %	84.3	88.3
Production %	70.0	86.3

This shows that the newly prepared koechlinite is an active and selective catalyst for the ammoxidation of propene, with low ammonia combustion activity.

At a reaction temperature of 445°C and at the same residence time the feed composition was then changed to the following conditions in mole%:

C_3H_6 5.3, NH_3 2.9, O_2 5.4, H_2O 6.7, He 79.7.

According to equation (2) we operated this time with deficits in oxygen and ammonia. Lower propene conversions were observed and the catalyst reacted during 8 hr to give a reduced state. The following data were obtained:

	C_3H_6	NH_3
Conversion %	63.5	97.0
Selectivity %	75.7	91.4
Production %	48.1	88.6

TABLE 1

FEED AND PRODUCT COMPOSITION AT 445°C

	Feed in mmole min^{-1}	Products in mmole min^{-1}
O_2	1.135	0.003
N_2	0.020	0.038
NH_3	0.575	0.013
C_3H_6	0.709	0.121
H_2O	0.889	2.728
CO		0.027
CO_2		0.140
C_2H_4O		0.006
C_3H_4O		0.004
CH_3CN		0.049
C_3H_3N		0.496

After complete reoxidation of the catalyst, which proceeded rather slowly and after starting the acrylonitrile production again, we surprisingly observed an enhanced ammonia combustion. Obviously the reduced catalyst is not able to resist prolonged heating at 445°C. From this experiment we learned never to operate with a deficit in oxygen.

Let us now discuss these results. If we consider the pH during slurry reaction as an indication of the degree to which koechlinite formation proceeds, then one might conclude that in the first run of 20 hr boiling and stirring the inorganic reaction proceeded to more than 90% (compare the pH from 7 to 2 in the first run with the pH from 7 to 3.5 in the second run).

The unreacted $BiONO_3$ and H_2MoO_4 in our previous preparation (*1*) might have been the origin of complications in the ammoxidation. During further calcination probably for a major part they react further also with koechlinite formation, but the possibility remains that small amounts of Bi_2O_3 and MoO_3 are formed. For 1-butene oxidation these contaminations are harmless, but they are detrimental for the ammoxidation of propene, because of the high ammonia combustion. With our improved preparation we avoided formation of contaminations and it is shown that a good acrylonitrile catalyst is obtained for this small fixed bed process with yields around 70% in one run and with a low ammonia combustion.

Now we have to discuss the reappearance of ammonia combustion on the catalyst which has been operating for 8 hr in a reduced state and which was reoxidized. Grasselli *et al.* (*5*) reported some time ago that their Bi/Mo catalyst for a short time could operate in a reduced state, but they did not mention the danger which is involved if such operations are continued for longer time. To explain why during such operations for a period of hours the reoxidation property of the catalyst is becoming worse and why suddenly ammonia combustion appears again, we appeal to the well known thermal instability of divalent bismuth:

$$3Bi^{++} \rightarrow Bi^0 + 2Bi^{3+} \tag{3}$$

If such a reaction occurs in the Bi_2O_2 layer of reduced koechlinite and if the reduced catalyst is not immediately reoxidized [see Batist *et al.* (*6*)] or cooled down directly, it means that above 400°C Bi-atoms can leave their position in the layer and after joining together they are slowly reoxidized to Bi_2O_3 conglomerates; hence the return of ammonia combustion. Formation of these conglomerates from the original Bi_2MoO_6 phase will be accompanied by formation of MoO_3 clusters and it is likely that they also participate the ammonia combustion.

We may conclude that all the efforts which have been made during preparation to avoid formation of these contaminations are wasted by this experiment with a deficit of oxygen in the feed and the result is that we obtained our old sample again.

That formation of Bi atoms during prolonged heating of reduced catalysts is indeed highly probable, has been shown by J. F. H. Bouwens of our laboratory (unpublished). With X-ray measurements he showed that Bi metal is already observable after 3 hr heating of reduced koechlinite in an atmosphere where oxygen is absent. Furthermore, during reduction of koechlinite with 1-butene in a Stanton balance, he found a fast process proceeding to Bi_2MoO_5 followed by a much slower reduction to further reduced states. It will be clear that these findings will have some consequences with respect to earlier reported work. For instance, Matsuura and Schuit (*7*) in all their adsorption measurements on reduced Bi molybdates have used reduced catalysts which were subsequently heated for 3 hr. The consequences therefore are:

(1) The quadratic loss of B centers, described by them as the result of reduction, is probably merely caused by heat treatment.

(2) The slow reoxidations with an activation energy of O diffusion of 28 kcal mole^{-1} reported by them are also obviously affected by heat treatment. This is now confirmed by Matsuura himself in a new experiment where reduced catalysts immediately were reoxidized. Now he observed fast reoxidations with an activation energy for oxygen diffusion of 13 kcal mole^{-1}. Actually this is a confirmation of suggestions given earlier (*6*, *8*).

Irrespective of these comments, we are convinced that by their adsorption measurements Matsuura and Schuit (*7*) have done excellent work in their attempt to develop a surface site model for selective oxidation reactions.

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