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Reduction of Bi_2O_3-MoO_3 Catalyst during the Ammoxidation of Propylene in the Absence of Gaseous Oxygen

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The reduction of a P_2O_5-Bi_2O_3-MoO_3/SiO_2 catalyst (a catalyst for the acrylonitrile process), consisting of $Bi_2O_3 \cdot 3MoO_3 + BiPO_4 +$ amorphous SiO_2, during the ammoxidation of propylene to acrylonitrile in the absence of gaseous oxygen was studied quantitatively by X-ray diffraction techniques and by catalytic activity measurements. Amorphous SiO_2 and $BiPO_4$ are not affected in synthesis. The overall reduction of catalytically active $Bi_2O_3 \cdot 3MoO_3$ to metallic Bi and MoO_2 proceeds according to the following two consecutive reactions, where $Bi_2O_3 \cdot MoO_3$ (koechlinite) is an intermediate:

$$Bi_2O_3 \cdot 3MoO_3 \xrightarrow{(C_3H_6, NH_3)} Bi_2O_3 \cdot MoO_3 + 2\,MoO_2 + O_2$$

$$Bi_2O_3 \cdot MoO_3 \xrightarrow{(C_3H_6, NH_3)} 2\,Bi + MoO_2 + 2\,O_2$$

The catalytic activity decreases rapidly with the increasing reduction of the catalyst. The phase changes of the catalyst and the product formation in synthesis correspond quantitatively to the depletion of lattice oxygen from the catalyst. In the absence of gaseous oxygen, the optimum activity for acrylonitrile of silica supported Bi_2O_3-MoO_3 catalysts is at a Bi:Mo atomic ratio of about 1.

For the catalytic ammoxidation of propylene to acrylonitrile on Bi_2O_3-MoO_3 based catalysts, a steady state mechanism involving simultaneous reduction and reoxidation of the catalyst surface with gaseous oxygen is suggested.

INTRODUCTION

Some Bi_2O_3-MoO_3 compositions are used as catalysts for the heterogeneous selective oxidation of unsaturated hydrocarbons. The most significant industrial application is the direct synthesis of acrylonitrile from propylene, ammonia, and air (ammoxidation) over a silica-supported P_2O_5-Bi_2O_3-MoO_3 catalyst (*1, 2*):

$$CH_2{=}CH{-}CH_3 + NH_3 + \tfrac{3}{2}O_2 \rightarrow CH_2{=}CH{-}CN + 3\,H_2O$$

Kolchin *et al.* studied the effect of some additives to catalyst and published a literature survey (*3, 4*). Dalin *et al.* (*5*) found a sharp decline in catalyst activity when there is insufficient oxygen in the feed gas and suggested the possibility of oxygen from the catalyst entering into the reaction thereby changing the composition of the oxide catalyst. Leclercq (*6*) reported the preparation of unsaturated nitriles from olefins and ammonia (without gaseous oxygen) over a catalyst consisting of a mass of oxides of arsenic, bismuth, and molybdenum. In this case, the catalyst was regenerated periodically, due to the reduction of the oxide mass, thereby causing it to progressively lose its activity. Similar findings were reported by Eygen *et al.* (*7*) using antimonates of various elements. Ammoxidation of propylene to acrylonitrile in the absence of gaseous oxygen over a P_2O_5-Bi_2O_3-MoO_3/SiO_2 catalyst was observed by Malhotra of this Laboratory (*8*).

From these references it appears that Bi_2O_3-MoO_3 based compositions act as catalysts and as reagents (presumably entering into the reaction) during the ammoxidation of propylene without gaseous oxygen. Hence significant changes in the phase composition and activity of the catalyst with the decreasing concentration of gaseous oxygen in the feed gas are to be expected. However, there is no evidence in the literature for a systematic study of this problem of industrial and scientific importance. This study was undertaken to establish quantitatively the phase changes of the catalyst taking place in synthesis without gaseous oxygen and to correlate these changes with the activity and selectivity of the catalyst.

EXPERIMENTAL PROCEDURE

Phase compositions of the catalyst samples were determined from X-ray diffraction patterns obtained with a Norelco diffractometer using Ni filtered Cu $K\alpha$ radiation. A Tem-Pres SX-2BR diffractometer furnace (Tem-Pres Research Inc., State College, Pennsylvania) equipped with a temperature programmer and recorder was used for phase studies at elevated temperatures.

For crystallographic characterization of $Bi_2O_3 \cdot MoO_3$ and $Bi_2O_3 \cdot 3MoO_3$, precise interplanar spacings were determined from Guinier patterns made with a Hägg camera (80-mm diameter, transmission-type, evacuated, and equipped with a quartz monochromator) with Cu $K\alpha_1$ radiation and using KCl as an internal standard. The integrated relative intensities were obtained from diffractometer patterns using Ni-filtered Cu $K\alpha$ radiation and by planimetering the peak areas.

Most of the catalytic activity tests were conducted in single-stage fluid-bed reactors using 100-cm^3 catalyst of 60–200 mesh particle size. The reactors were 19 inches long and were constructed from 1-inch type 304 stainless steel pipe. They contained a feed gas line on the bottom, an off-gas line on the top, a catalyst filling port, and three thermocouple wells. Inside the reactors, two 500-mesh stainless steel screens (placed 17 inches apart) served as gas distributor and catalyst entrainment screens. Some fixed-bed activity tests were done in $\frac{1}{2}$-inch ID stainless steel U-tube reactors using 30-cm^3 catalyst of $\frac{3}{16}$-inch pellets.

The reactors were placed in a molten salt bath and connected to on-line analytical equipment by means of heated off-gas lines. A Consolidated Electrodynamics Corp. Model 21-620 mass spectrometer was used to analyze for C_3H_6 and NH_3 in the feed gas and C_3H_6, acrylonitrile, and CO_2 in the product gas. A Perkin-Elmer Model 154 vapor-phase chromatograph was used to analyze for acrylonitrile, acetonitrile, and NH_3 in the off-gas. A 4 $\frac{1}{2}$-ft column packed with 10% Quadrol on Porapak-Q was used at 120°C. The feed gas flow rates were measured by means of a calibrated flow meter and reported as Volume Hourly Space Velocity which is defined as the volume of total feed gas at NTP per unit volume of catalyst per hours. All of the runs were made under isothermal conditions and at atmospheric pressure.

RESULTS AND DISCUSSION

A. Phases in the System Bi_2O_3-MoO_3

For this study, crystallographic data for compounds of Bi_2O_3 and MoO_3 were necessary for the determination of phase compositions of the catalysts. The system Bi_2O_3-MoO_3 is the subject of a number of recent studies. Erman *et al.* (*9*) studied the system by X-ray diffraction using samples prepared by fusion of oxides at 750–900°C and samples prepared by heating of coprecipitates at 500°C. They found three compounds: two forms of $Bi_2O_3 \cdot MoO_3$ (form I of koechlinite structure and form II), $Bi_2O_3 \cdot 2MoO_3$, and $Bi_2O_3 \cdot 3MoO_3$. $Bi_2O_3 \cdot 2MoO_3$ is reported to be orthorhombic with $a = 10.79$, $b = 11.89$, and $c = 11.86$ Å, which is formed by a peritectic reaction (*10*, *11*). Doyle and Forbes (*12*) studied the system by the diffuse reflectance technique and reported 11 phases including $3Bi_2O_3 \cdot MoO_3$, $2Bi_2O_3 \cdot MoO_3$, $Bi_2O_3 \cdot MoO_3$, $Bi_2O_3 \cdot 2MoO_3$, and $Bi_2O_3 \cdot 3MoO_3$. They gave no X-ray data for these phases. Bleijenberg, Lippens, and Schuit (*13*) studied the system Bi_2O_3-MoO_3 by DTA and X-ray diffraction techniques and reported a phase diagram showing three compounds of Bi_2O_3 and MoO_3: $3Bi_2O_3 \cdot MoO_3$, $Bi_2O_3 \cdot MoO_3$(same as mineral koechlinite), and $Bi_2O_3 \cdot 3MoO_3$. They gave no X-ray data other than a collection of bar diagrams. Gattow (*14*) prepared $2Bi_2O_3 \cdot MoO_3$ by precipitation from aqueous

TABLE 1

X-RAY POWDER DIFFRACTION DATA FOR $Bi_2O_3 \cdot 3MoO_3$[a]

hkl	d_{obs}	d_{calc}	I_{obs}	hkl	d_{obs}	d_{calc}	I_{obs}	hkl	d_{obs}	d_{calc}	I_{obs}
011	7.888	7.887	15	230	2.580	2.581	1	242	1.881	1.881	23
100	6.972	6.971	23	042	2.542	2.542	2	$\bar{1}61$	1.860	1.860	3
$\bar{1}11$	6.290	6.290	9	$\bar{3}12$	2.511	2.511	8	$\bar{4}14$	1.853	1.853	6
110	5.962	5.964	3	202	2.485	2.485	14	233	1.840	1.840	5
020	5.759	5.758	6	$\bar{3}11$	2.446	2.446	1	115	1.831	1.831	2
002	5.412	5.412	6	231	2.348	2.348	3	$\bar{4}11$	1.826	1.826	4
021	5.084	5.084	6	$\bar{1}15$	2.328	2.328	6	$\bar{3}44$	1.808	1.808	4
$\bar{1}12$	5.033	5.032	2	300	2.325	2.324		006	1.804	1.804	9
012	4.899	4.898	36	$\bar{3}21$	2.296	2.296	2	214	1.775	1.775	1
$\bar{1}21$	4.569	4.569	11	310	2.278	2.278	5	125	1.765	1.765	9
120	4.443	4.439	2	043	2.250	2.250	6	$\bar{1}63$	1.729	1.728	5
$\bar{1}13$	3.758	3.758	6	142	2.247	2.247	8	410	1.723	1.723	
$\bar{2}11$	3.637	3.636	1	114	2.181	2.181	3	$\bar{3}52$	1.716	1.716	14
031	3.617	3.618	12	$\bar{1}52$	2.129	2.130	4	$\bar{4}25$	1.702	1.702	8
102	3.593	3.593	11	052	2.119	2.119	6	063	1.695	1.695	16
200	3.488	3.486	2	$\bar{3}33$	2.096	2.097	3	135	1.669	1.670	2
112	3.430	3.430	6	311	2.062	2.061	2	$\bar{4}31$	1.666	1.666	4
$\bar{1}31$	3.418	3.418	5	$\bar{1}35$	2.021	2.021	2	$\bar{2}27$	1.641	1.641	7
210	3.337	3.336	10	$\bar{2}44$	2.006	2.006	22	071	1.626	1.626	1
$\bar{1}23$	3.272	3.272	23	143	1.991	1.991	2	$\bar{1}46$	1.622	1.622	5
$\bar{2}21$	3.192	3.190	100	$\bar{3}25$	1.968	1.969	3	154	1.599	1.599	3
032	3.132	3.131	6	$\bar{1}06$	1.963	1.963	5	$\bar{4}42$	1.595	1.595	10
023	3.059	3.058	90	$\bar{2}16$	1.959	1.959	3	323	1.592	1.592	
040	2.879	2.879	87	152	1.939	1.939	2	171	1.562	1.562	2
$\bar{2}04$	2.797	2.797	18	$\bar{1}16$	1.935	1.935	2	421	1.555	1.555	8
$\bar{1}33$	2.762	2.762	2	250	1.922	1.922	3	046	1.529	1.529	8
140	2.661	2.661	4	$\bar{4}02$	1.916	1.916	16				
221	2.638	2.637	2	035	1.885	1.886	5				

[a] d_{obs}, From Guinier pattern ($\lambda = 1.54051$ Å); d_{calc}, based on monoclinic lattice parameters, $a = 7.719$ Å, $b = 11.516$ Å, $c = 11.985$ Å, and $\beta = 115°25'$; I_{obs}, integrated intensities from diffractometer pattern (Cu $K\alpha$ radiation).

solution, which has an oxygen-deficient CaF_2 structure with $a = 5.65$ Å.

It is apparent that the system Bi_2O_3-MoO_3 is not unequivocally described. In this study, compositions corresponding to 3:1, 1:1, and 1:3 by mole Bi_2O_3:MoO_3 were prepared by ball milling the proper mixtures of oxides, then pressing them into small discs with a hydraulic press. After a heat treatment at 625°C for 16 hr, they were again ball-milled, repressed, and heated an additional 20 hr at 625°C. X-Ray diffraction patterns of these products were evaluated. Our data for $3Bi_2O_3 \cdot MoO_3$ were in agreement with that of Bleijenberg *et al.* (*13*). Data for $Bi_2O_3 \cdot MoO_3$ were similar to form II $Bi_2O_3 \cdot MoO_3$ of Erman *et al.* (*9*). Blasse (*15*) reported a tetragonal high-temperature form of $Bi_2O_3 \cdot MoO_3$ with $a = 3.95$ and $c = 17.21$ Å, prepared by heating the mixture of oxides at 750°C. The X-ray pattern of our sample contained a number of reflections in addition to those given by Blasse which could not be indexed with his lattice parameters. These additional reflections were not changed by a further heat treatment at 800°C. Since compounds $3Bi_2O_3 \cdot MoO_3$ and $Bi_2O_3 \cdot MoO_3$ (form II) were not encountered in catalysts during this study, their crystallographic characterization was not attempted. Data for $Bi_2O_3 \cdot 3MoO_3$ were generally in good agreement with the data of Erman *et al.* (*9*) and Bleijenberg *et al.* (*13*). However, our X-ray pattern contained numerous additional reflections. By single-crystal studies, Mekhtiev *et al.* (*16*) found that $Bi_2O_3 \cdot 3MoO_3$ is structurally related to scheelite and it is monoclinic with $a = 7.89$, $b = 11.70$, $c = 12.24$, Å and $\beta = 116°20'$. They gave no X-ray powder diffraction data.

A 1:3 by mole Bi_2O_3:MoO_3 composition was also prepared by evaporation of an acidified (HNO_3) aqueous solution of $Bi(NO_3)_3 \cdot 5H_2O$ + $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$. The dried residue was heat-treated for 16 hr at 500°C then ball-milled and heated for 20 hr at 600°C. It is an off-white colored powder, m.p. 665°C. Its X-ray pattern was identical to $Bi_2O_3 \cdot 3MoO_3$ prepared starting from the oxides. The Guinier pattern could not be indexed satisfactorily with the lattice parameters of Mekhtiev *et al.* (*16*). However, the pattern was completely indexed on the basis of computer-refined monoclinic lattice parameters of $a = 7.719$, $b = 11.516$, $c = 11.985$ Å, and $\beta = 115°25'$. The results are shown in Table 1. On the basis of four $Bi_2O_3 \cdot 3MoO_3$ per unit cell, its theoretical density is calculated to be 6.197 g/cm^3 in comparison to its observed density of 6.14 g/cm^3 at 25°C, obtained by the pycnometer method.

A sample of synthetic koechlinite ($Bi_2O_3 \cdot MoO_3$) was prepared by a technique similar to one used by Erman *et al.* (*9*). A 1:1 by mole Bi_2O_3:MoO_3 composition was prepared by adding a solution of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in 1:1 by volume conc. NH_4OH:H_2O into an acidified (HNO_3) aqueous solution of $Bi(NO_3)_3 \cdot 5H_2O$, kept for 1 hr at ~80°C at pH 8, evaporated after adjusting to pH 11 with conc. NH_4OH, and the residue heated for 20 hr at 500°C. It is a yellow powder, m.p. 933°C. The Guinier pattern was indexed on the basis of computer-refined orthorhombic lattice parameters of $a = 5.502$, $b = 16.213$, and $c = 5.483$ Å. These lattice parameters are in excellent agreement with those reported by Zemann (*17*) for the mineral koechlinite. The results are shown in Table 2. On the basis of four $Bi_2O_3 \cdot MoO_3$ per unit cell, its theoretical density is calculated as 8.281 g/cm^3 in comparison to its pycnometric density of 8.26 g/cm^3 at 25°C.

Kolchin *et al.* (*18*) reported the formation of a stable compound $2Bi_2O_3 \cdot 3MoO_3 \cdot P_2O_5$, by introduction of phosphorus into bismuth molybdates. However, our inspection of their unindexed X-ray data revealed a close match for a mixture of the high-temperature form $BiPO_4$ (*19*) and $Bi_2O_3 \cdot 3MoO_3$. Therefore,

TABLE 2

X-RAY POWDER DIFFRACTION DATA FOR $Bi_2O_3 \cdot MoO_3$ (SYNTHETIC KOECHLINITE)[a]

hkl	d_{obs}	d_{calc}	I_{obs}	*hkl*	d_{obs}	d_{calc}	I_{obs}
020	8.094	8.107	15	202	1.942	1.942	17
021	4.538	4.542	1	260	1.927	1.928	10
111	3.776	3.777	3	062	1.925	1.925	17
041	3.259	3.259	2	222	1.889	1.889	2
131	3.153	3.154	100	023	1.783	1.783	1
200	2.750	2.751	16	311	1.730	1.729	1
002	2.741	2.742	18	113	1.724	1.725	1
060	2.701	2.702	16	172	1.684	1.684	1
220	2.604	2.605	3	331	1.656	1.656	13
022	2.597	2.597		133	1.652	1.652	19
151	2.489	2.489	8	191	1.634	1.634	18
112	2.426	2.426	2	082	1.630	1.630	2
221	2.353	2.353	1	262	1.577	1.577	13
240	2.276	2.276	3	351	1.533	1.533	1
042	2.270	2.271		153	1.530	1.529	2
132	2.241	2.233	<1	312	1.518	1.518	<1
241	2.099	2.102	<1	223	1.496	1.496	1
080	2.027	2.027	<1	243	1.425	1.425	1
152	1.957	1.957	1	282	1.402	1.402	1

[a] d_{obs}, From Guinier pattern ($\lambda = 1.54051$ Å); d_{calc}, based on orthorhombic lattice parameters, $a = 5.502$ Å, $b = 16.213$ Å, and $c = 5.483$ Å; I_{obs}, integrated intensities from diffractometer pattern (Cu $K\alpha$ radiation).

a 1:2:3 by mole $P_2O_5:Bi_2O_3:MoO_3$ composition was prepared from solution by evaporation and by heating the residue 16 hr at 600°C. It contained only $Bi_2O_3 \cdot 3MoO_3$ plus high-temperature form $BiPO_4$; a new phase could not be detected. Obviously, Kolchin *et al.* were dealing with a mixture, not with a new phase.

B. Preparation and Characterization of the Catalyst

In this study a 70% 1:9:24 by mole $P_2O_5:Bi_2O_3:MoO_3$ + 30% SiO_2 catalyst, a catalyst for the acrylonitrile process, described in the patent literature (*1*), was used. It was prepared by the following procedure:

An acidified (HNO_3) aqueous solution of $Bi(NO_3)_3:5H_2O$ was added under vigorous agitation to an aqueous colloidal silica* containing H_3PO_4 and molybdic acid and then ball-milled for 1 hr. After evaporating on a steam bath it was dried for 16 hr at 130°C. The material was ground, screened to collect 60–200 mesh portion, and heated in air for 16 hr at 540°C.

The BET surface area of this catalyst was 30 m^2/g. The irregularly shaped grains had a homogeneous appearance, as observed from photomicrographs. Transmission electron micrographs indicated that the catalyst grains were composed of fairly transparent, uniform round particles of about 0.015-μ size and nontransparent, irregularly shaped particles in the approximate range of 0.05–0.30 μ. The particles fairly transparent to electron beam are amorphous SiO_2. The nontransparent particles are apparently P_2O_5-Bi_2O_3-MoO_3 compositions. Phase analysis of the catalyst by X-ray diffraction indicated only a large amount of $Bi_2O_3 \cdot 3MoO_3$ plus a small amount of the high-temperature form of $BiPO_4$ (*19*), except for a barely detectable trace of $Bi_2O_3 \cdot MoO_3$ (koechlinite). The X-ray pattern had no unidentified peaks nor any amorphous bands.

The following compositions were prepared by the same procedure used for the catalyst preparation in order to examine the phase composition in the absence of SiO_2 and phosphorus: (I) 1:9:24 by mole $P_2O_5:Bi_2O_3:MoO_3$, (II) 9:24 by mole $Bi_2O_3:MoO_3$. Compositions I and II contained, respectively, a large amount of $Bi_2O_3 \cdot 3MoO_3$, a small amount of the high-temperature form of $BiPO_4$, plus a trace of koechlinite; and a large amount of $Bi_2O_3 \cdot 3MoO_3$ plus a small amount of koechlinite. Aqueous colloidal silica after evaporation, drying, and heating for 16 hr at 540°C was amorphous and had only a very broad band ($d \approx 4.1$ Å) on its X-ray pattern. Calculations showed that this amorphous band of SiO_2 could not be detected in the X-ray pattern of the actual catalyst due to the high mass absorption coefficient (for X-rays) of catalyst. On the basis of this and electron micrographs, it is conclusive that SiO_2 is in an amorphous state in the catalyst.

In a high-temperature X-ray diffraction study of the catalyst in air in the temperature range of 25–600°C, no chemical or crystallographic phase changes were observed. Therefore, the phase composition of the catalyst at synthesis temperature is the same as at room temperature.

C. Reduction of the Catalyst in Synthesis

The ammoxidation of propylene to acrylonitrile in the absence of gaseous oxygen was studied using the 70% 1:9:24 by mole $P_2O_5:Bi_2O_3:MoO_3$ + 30% SiO_2 catalyst in a fluid-bed reactor with a feed gas of 5.1% C_3H_6, 5.1% NH_3, and 89.8% N_2, at 450°C, and 340 hr^{-1} volume hourly space velocity. Using 100 cm^3 of fresh catalyst for each run, syntheses of 10-, 30-, 60-, 90-, 115-, and 180-min duration were made. During each run, the reactor off-gas was monitored periodically for C_3H_6, NH_3, acrylonitrile, acetonitrile, and CO_2 to determine the catalytic activity and selectivity as a function of time in synthesis. At the conclusion of each run, the catalyst was removed from the reactor after cooling to room temperature in a N_2 atmosphere and its phase composition was determined by X-ray diffraction.

Since the catalytic data obtained from all of these runs were similar, only the results of a 180-min run are shown in Figs. 1 and 2. The

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* Ludox LS Colloidal Silica, from Industrial and Biochemicals Dept., E. I. du Pont de Nemours & Co. It contains 30.3% SiO_2, 0.1% Na_2O; approximate colloidal particle diameter 15–16 mμ.

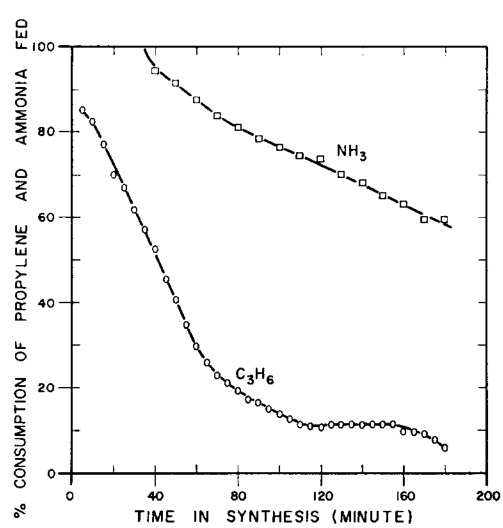

FIG. 1. Feed gas consumption over P_2O_5-Bi_2O_3-MoO_3/SiO_2 catalyst (5.1% C_3H_6, 5.1% NH_3, 89.8% N_2; 450°C; 340 hr^{-1} volume hourly space velocity).

catalytic activity is at a maximum with the fresh catalyst, then declines sharply with increasing time in synthesis. Consumption of C_3H_6 first decreases nearly linearly with time and more rapidly than NH_3, then it slows down (Fig. 1). In a separate experiment, by passing an NH_3 plus argon mixture over the catalyst, a complete oxidation of NH_3 according to the following reaction was observed:

$$2\,NH_3 + \tfrac{3}{2}O_2 \rightarrow N_2 + 3\,H_2O \qquad (1)$$

Conversion of C_3H_6 to the main products acrylonitrile, acetonitrile, and CO_2 was calculated on the basis of the following assumed overall reactions:

$$C_3H_6 + NH_3 + \tfrac{3}{2}O_2 \rightarrow C_3H_3N + 3\,H_2O \qquad (2)$$

$$C_3H_6 + NH_3 + \tfrac{5}{2}O_2 \rightarrow C_2H_3N + CO_2 + 3\,H_2O \qquad (3)$$

$$C_3H_6 + \tfrac{9}{2}O_2 \rightarrow 3\,CO_2 + 3\,H_2O \qquad (4)$$

Conversion to acrylonitrile is at a maximum with the fresh catalyst and stays at this level for a short time, then declines rapidly (Fig. 2). Interestingly, after about 60 min no acetonitrile could be detected. Small amounts of CO and HCN were also found in the product gas, but were not monitored in these experiments. The carbon content of each used catalyst sample was determined by a microcombustion technique. Carbon deposition on the catalyst increases steadily with time in synthesis (Fig. 3).

The used catalysts were black. Phase analysis of these catalysts indicated that the high-temperature form of $BiPO_4$ was not affected in synthesis under the conditions of these experiments. $Bi_2O_3{\cdot}3MoO_3$ was reduced to metallic Bi and MoO_2 as the final phases. During this reduction, $Bi_2O_3{\cdot}MoO_3$ (koechlinite) was formed as an intermediate phase. No other intermediate phases were detected. By this reduction, the elemental composition of the catalyst changes (loss of oxygen), resulting in a change of the X-ray mass absorption coefficient of the catalyst. For fresh and fully reduced catalysts, the mass absorption coefficients (for Cu *Kα*) were calculated to be 127 and 135 cm^2/g, respectively. By neglecting this small change of mass absorption coefficient, the X-ray diffraction intensity becomes directly

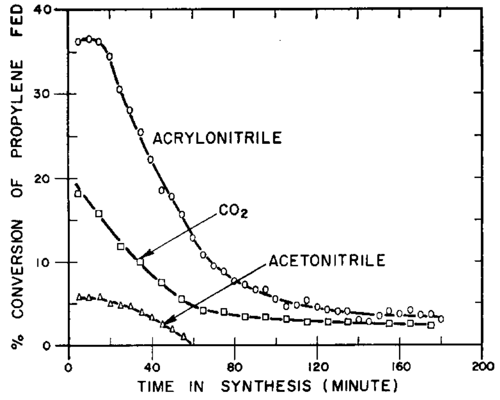

FIG. 2. Conversion to main products over P_2O_5-Bi_2O_3-MoO_3/SiO_2 catalyst (for conditions see Fig. 1).

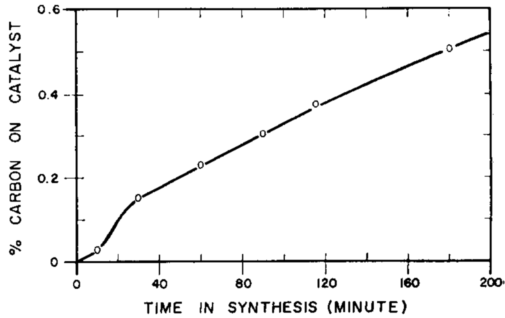

FIG. 3. Carbon deposition on P_2O_5-Bi_2O_3-MoO_3/SiO_2 catalyst (for conditions see Fig. 1).

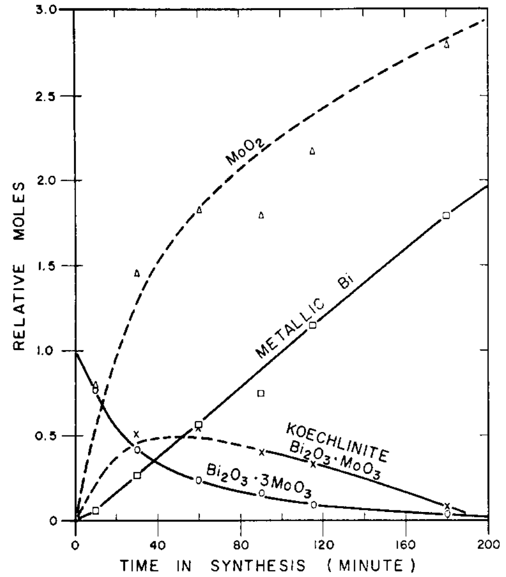

FIG. 4. Reduction of $Bi_2O_3 \cdot 3MoO_3$ of P_2O_5-Bi_2O_3-MoO_3/SiO_2 catalyst in synthesis (for conditions see Fig. 1).

proportional to concentration. For quantitative phase analysis, the peak heights of the (023), (014), (131), and (110) reflections were used for $Bi_2O_3 \cdot 3MoO_3$, Bi, koechlinite, and MoO_2, respectively. Concentrations were calculated as relative moles normalized on the basis of 1 mole of $Bi_2O_3 \cdot 3MoO_3$. The results are shown in Fig. 4. The concentration profiles shown in solid lines were entirely based on a best fit to the experimental data points. The profiles shown in dashed lines were calculated from a material balance and they are in satisfactory agreement with the experimental data points. The overall chemical phase changes of $Bi_2O_3 \cdot 3MoO_3$ in synthesis (Fig. 4) are explained by the following two consecutive reactions:

$$Bi_2O_3 \cdot 3MoO_3 \xrightarrow{C_3H_6,NH_3} \underset{\text{(koechlinite)}}{Bi_2O_3 \cdot MoO_3} + 2\,MoO_2 + O_2 \qquad (5)$$

$$\underset{\text{(koechlinite)}}{Bi_2O_3 \cdot MoO_3} \xrightarrow{C_3H_6,NH_3} 2\,Bi + MoO_2 + 2\,O_2 \qquad (6)$$

Since $BiPO_4$ and amorphous SiO_2 are not affected and only $Bi_2O_3 \cdot 3MoO_3$ is reduced in synthesis, the "available O_2" content of this particular catalyst was calculated (on the basis of $Bi_2O_3 \cdot 3MoO_3 \rightarrow 3\ O_2$) as 0.215 moles O_2 per 100 g catalyst. Depletion of oxygen from the catalyst, as a function of time in synthesis, was obtained in three different ways:

(1) Oxygen depletion was calculated on the basis of phase compositions of used catalysts (Fig. 4) obtained from X-ray data.

(2) The amount of oxygen given off from the catalyst was calculated from the NH_3 consumption and the main reaction products (Figs. 1, 2) assuming the reactions (1)–(4).

(3) A small portion of each used catalyst was heated in air for 18 hr at 550°C and the weight increase was measured. Complete oxidation of the samples was confirmed by X-ray diffraction. After a correction for the carbon content of each sample, the oxygen uptake or the oxygen depletion of the catalyst was determined. The results are shown in Fig. 5. The agreement of oxygen depletion determined gravimetrically, with the depletion calculated from X-ray data and from the main reaction products is very good.

By microscopic inspection of used catalysts, separation of metallic Bi (molten at the synthesis temperature, m.p. 271°C) from the catalyst grains was not observed. It is apparently held in the pores of the amorphous SiO_2 matrix. The used catalysts were regenerated with an air and N_2 mixture at 450–500°C, restoring the initial phase composition and the catalytic activity

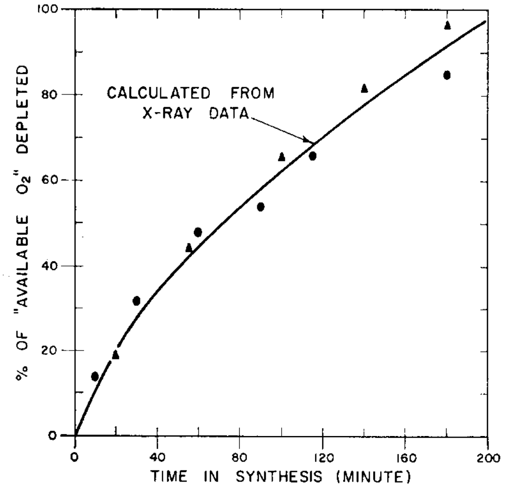

FIG. 5. Oxygen depletion of P_2O_5-Bi_2O_3-MoO_3/SiO_2 catalyst in synthesis; ●, determined gravimetrically; ▲, calculated from reaction products (for conditions see Fig. 1).

of the catalyst. As intermediate phases of regeneration reactions, only β-Bi_2O_3 (*20*), MoO_3, and koechlinite were detected. Therefore, during the regeneration, carbon (coke) is burned off, metallic Bi and MoO_2 are oxidized to β-Bi_2O_3 and MoO_3, respectively, and finally $Bi_2O_3 \cdot 3MoO_3$ is formed by solid state reactions. Koechlinite is apparently an intermediate in the formation of $Bi_2O_3 \cdot 3MoO_3$ during the regeneration.

A comparison of Figs. 1–5 indicates that the rapid decline of activity with time is apparently caused by a combination of the depletion of lattice oxygen (requiring oxygen ion diffusion in the solid), deposition of carbon, and the phase changes of the catalyst. The product formation and the phase changes of the catalyst correspond quantitatively to the depletion of lattice oxygen from the catalyst (Fig. 5). By the reduction of P_2O_5-Bi_2O_3-MoO_3/SiO_2 catalyst with $C_3H_6 + NH_3$, the same products are formed as by the catalytic reaction of $C_3H_6 + NH_3 + O_2$ over the same catalyst. Therefore, it is suggested that the catalytic ammoxidation of propylene to acrylonitrile proceeds by a steady state mechanism in which the catalyst surface simultaneously reduces and reoxidizes with gaseous oxygen. These results agree with the recent literature. Batist, Kapteijns, Lippens, and Schuit (*21*), reported that the reduction of Bi_2O_3-MoO_3 catalyst by 1-butene proceeds to MoO_2 and Bi. In their extensive studies, using a mathematical model for a surface reaction followed by oxygen vacancy diffusion in the solid, they concluded that the catalytic oxidation of 1-butene consists of a surface reaction followed by a reoxidation with gaseous oxygen. Bhattacharyya, Janakiram, and Ganguly (*22*), from kinetic studies, reported a similar mechanism for the oxidation of methanol on V_2O_5. Levy (*23*) reported the variation of the oxidation state in bulk of a cobalt oxide catalyst with reaction conditions during the oxidation of butane. Correlations between the catalytic activity of metal oxides in hydrocarbon oxidation and metal–oxygen bond strength have been reported (*24–26*).

D. Catalytic Activity vs. Composition in the System Bi_2O_3-MoO_3

There are recent investigations, carried out in the presence of gaseous oxygen. Kolobikhin and Emel'yanova (*27*) studied the oxidative dehydrogenation of butenes to 1,3-butadiene over Bi_2O_3-MoO_3 catalysts supported on silica gel and concluded that the optimal catalyst composition corresponds to a Bi:Mo atomic ratio of 0.7–0.9. Batist, Lippens, and Schuit (*28*) reported the maximum activity at a Bi:Mo atomic ratio of about 1 for the oxidative dehydrogenation of 1-butene to butadiene over unsupported Bi_2O_3-MoO_3 catalysts. They found $Bi_2O_3 \cdot 3MoO_3$ to be almost inactive. For the ammoxidation of propylene to acrylonitrile in the presence of gaseous oxygen, Gel'bshtein *et al.* (*29*) found optimal activity at a Bi:Mo atomic ratio of 1 using unsupported Bi_2O_3-MoO_3 catalysts.

In this study, the catalytic activity for the ammoxidation of propylene to acrylonitrile without gaseous oxygen was studied as

TABLE 3

CATALYSTS WITH VARYING Bi:Mo RATIO

Designation[a]	Composition		Heat treatment		Phases present
	Bi:Mo atomic ratio	% SiO_2	hr	°C	
A	Bi_2O_3 only	0	1	500	α-Bi_2O_3
B	4:1	30	16	375	$2Bi_2O_3 \cdot MoO_3$[b]
C	2:1	30	16	540	Koechlinite[b]
D	4:3	30	16	500	Koechlinite + small $Bi_2O_3 \cdot 3MoO_3$[b]
E	1:1	30	16	500	Koechlinite + $Bi_2O_3 \cdot 3MoO_3$[b]
F	2:3	30	16	540	$Bi_2O_3 \cdot 3MoO_3$[b]
G	MoO_3 only	30	16	540	MoO_3[b]

[a] A, c.p. grade Bi_2O_3 formed into $\frac{3}{16}$-inch pellets; B–G, prepared from solution using Ludox LS, 60–200 mesh fluid-bed catalysts.

[b] SiO_2 was amorphous.

TABLE 4

DECOMPOSITION OF ACRYLONITRILE IN THE ABSENCE OF GASEOUS OXYGEN[a]

Catalyst	% Consumption of acrylonitrile fed[b]	Major products[c]
A (Bi_2O_3)	92	CO_2, acetonitrile
C (Bi:Mo = 2:1, 30% SiO_2)	6	CO_2, acetonitrile
F (Bi:Mo = 2:3, 30% SiO_2)	2	CO_2
G (MoO_3, 30% SiO_2)	0	—
G[d]	56[e]	Mainly "coke" + CO_2, acetonitrile, propionitrile
70% 1:9:24 mole P_2O_5:Bi_2O_3:MoO_3 + 30% SiO_2	11	CO_2, acetonitrile
Amorphous SiO_2	0	—
None (empty reactors)	0	—

[a] Feed gas, 4% acrylonitrile in helium; 460°C; 340 hr^{-1} volume hourly space velocity.

[b] Average of 40 min runs.

[c] Reactor effluent gas was not analyzed for CO.

[d] After complete reduction of MoO_3 to MoO_2 with a 40% NH_3, 60% N_2 gas at 460°C, 340 hr^{-1} volume hourly space velocity.

[e] First 5 min; consumption decreased to 4% at 35 min.

a function of composition in the system Bi_2O_3-MoO_3. The catalysts used are described in Table 3. Activity tests were done with a feed gas of 4.6% C_3H_6, 6.8% NH_3, 88.6% N_2, at 450°C, and 170 hr^{-1} volume hourly space velocity. Under the conditions of these experiments, pure amorphous SiO_2 (used as a support in the fluid-bed catalysts) was practically inert. With the catalysts shown in Table 3, the average percent conversion to acrylonitrile for the initial 20-min period of each run was plotted as a function of mole % MoO_3 in the Bi_2O_3-MoO_3 composition. The results are shown in Fig. 6. The main reaction product over Bi_2O_3 was CO_2 with a trace of acetonitrile but no acrylonitrile. MoO_3 has low activity. In the 50–75 mole % MoO_3 region, including the compounds koechlinite and $Bi_2O_3 \cdot 3MoO_3$, there is high activity. The optimum activity for conversion of propylene to acrylonitrile in the absence of gaseous oxygen, is at a Bi:Mo atomic ratio of about 1 (catalyst E in Fig. 6). This is an excellent agreement with the results obtained by the presence of gaseous oxygen (*29*). At this ratio, the catalyst contained a mixture of koechlinite and $Bi_2O_3 \cdot 3MoO_3$; a $Bi_2O_3 \cdot 2MoO_3$ (*10*) phase was not observed.

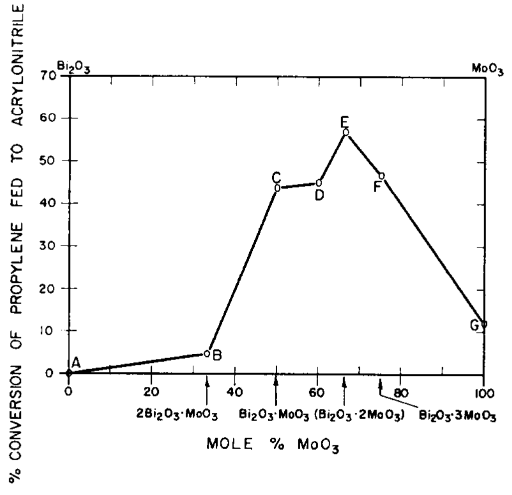

FIG. 6. Conversion to acrylonitrile as a function of composition in the system Bi_2O_3-MoO_3 (4.6% C_3H_6, 6.8% NH_3, 88.6% N_2; 450°C; 170 hr^{-1} volume hourly space velocity).

The decomposition of acrylonitrile in the absence of gaseous oxygen was briefly investigated by passing a gas of 4% acrylonitrile in helium over various catalysts at 460°C, 340 hr^{-1} volume hourly space velocity. The results are shown in Table 4. By a comparison of Table 4 with Table 3 and Fig. 6, it is seen that catalysts with high selectivity for acrylonitrile gave low decomposition. Amorphous SiO_2 and MoO_3 are inert to acrylonitrile. Acrylonitrile decomposes greatly on Bi_2O_3. Decomposition of acrylonitrile on noncarbonized MoO_2 is very high initially, then decreases rapidly with the increasing deposition of large amounts of carbon on the MoO_2 catalyst. Naumov, Balandin, Tolstopyatova, and Korytnyi (*30*) reported similar results for the decomposition of alcohols on MoO_2.

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