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Compound Oxides Present in Vanadium–Molybdenum Oxide Maleic Catalysts*

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The composition and physical properties of two new compound oxides of vanadium and molybdenum have been determined. These have been shown to be major components of typical vanadium–molybdenum oxide catalysts such as are used commercially for oxidation of benzene to maleic anhydride. However, the pure crystalline compounds are not as active as commercial catalysts.

INTRODUCTION

To help understand the behavior of a catalyst, it is desirable to have as thorough an understanding of the chemistry of the catalyst as possible. The most widely used catalysts for oxidation of benzene to maleic anhydride are vanadium oxide–molybdenum oxide catalysts, sometimes containing small amounts of other oxides (*1–4*). The catalysts used in the kinetic studies made by our group were of this type (*5*).

While a considerable amount of work has been done on the vanadium-oxygen system, comparatively little definitive work has been done on the vanadium-molybdenum-oxygen system. The only previous work is that reported by Magneli and Oughton (*6*) that by Magneli and Blomberg (*7*), that by Tarama, Teranishi, and Yasui (*8*), and that by Ioffe, Ezhkova, and Lyubarskii (*9*). These workers discovered that phases other than V_2O_5 and MoO_3 are formed but failed to establish their nature or composition. This system has therefore been further investigated.

EXPERIMENTAL

Samples of varying vanadium-molybdenum-oxygen ratios were prepared by three different methods. In the first, mixtures of the dry finely powdered oxides having mole ratios varying from V_2O_5:MoO_3 to V_2O_5:$2MoO_3$ were prepared by carefully weighing the required amounts of the pure oxides and thoroughly mixing them. The mixtures were then sealed in evacuated silica glass tubes and heated to 600°C for periods ranging up to 2 weeks. The sample tubes were removed from the furnace at intervals and shaken to mix the oxides during the reaction period. Some sintering occurred but the mixture could usually be broken up by shaking or rapping the tube on the table. In the second, the required amounts of V_2O_5 and MoO_3 were weighed, mixed, and placed in a platinum crucible which was then heated by induction in air to approximately 900°C. The melts were examined directly after rapid cooling to room temperature in some cases, in others they were held at 600°C for several days to complete the reaction and to develop a higher degree of crystallinity. In the third method of preparation, the oxides were weighed in the desired ratio and dissolved in a minimum amount of concentrated hydrochloric acid. The solution was evaporated to dryness leaving a mixture of chlorides, oxychlorides, and oxides which were scraped from the evaporating dish, placed in a platinum tray, and heated in air at 600°C for periods up to several days. Finally, some of the oxides prepared by these methods were used as catalysts for the oxida-

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tion of benzene to maleic anhydride, resulting in reduction of the original oxides to lower oxides.

The composition of the samples so prepared was investigated by several methods. First, powder-type X-ray diffraction patterns were used to determine how many phases were present. A Norelco X-ray diffractometer with a high intensity copper target tube, proportional counter, scaler-ratemeter and strip chart recorder was used to record diffraction patterns of the samples. The instrument was aligned according to the maker's instructions. Interplanar distances for substances such as V_2O_5 and MoO_3 for which data of high accuracy are available (*10*) agreed with the accepted values within 0.025 Å. Examination in polarized light using a petrographic microscope was used to supplement the X-ray diffraction method.

The oxygen loss during reaction of the V_2O_5 and MoO_3 was determined by fitting the reaction tube with a delivery tube and collecting the evolved gas by displacement of mercury in a graduated cylinder. The gases were not collected until the reaction temperature, 600°C, had been reached so that air expelled on heating from room temperature would not be included. Calculations based on the initial rate of oxygen evolution without correction for the fact that the temperature was below reaction temperature during most of the heat-up time indicate that error due to this procedure was less than 0.5% of the amount of oxygen collected. In addition, attempts were made to determine the oxygen loss by dissolving weighed samples of the reacted material in dilute sulfuric acid at low temperature and titrating the lower valent vanadium or molybdenum with standard permanganate potentiometrically. Results by this method appear to be high, apparently due to a small amount of reduction during the process of dissolving the samples. Since the error is constant, the percentage error for slightly reduced samples is high and that for considerably reduced ones is much lower. Permanganate titration data have, therefore, been used only for samples where there was considerable reduction.

Infrared spectra of the starting oxides and the compound oxides formed from them were recorded using a Perkin-Elmer model 221 spectrometer and preparing the samples in the form of KBr pressed discs or Nujol mulls.

The relative resistivity of the starting oxides and the compound oxides was measured by compressing 0.200 g of the powdered oxide sample between a steel anvil and plunger in a steel die lined with 3/8-inch ID × 7/16-inch OD Teflon tubing. A 10 000 lb load, equivalent to 100 000 lb/sq. inch pressure on the sample, was applied using a small hydraulic press. The resistance between the anvil and plunger was measured with the sample under pressure using a DC Wheatstone bridge and electronic null detector.

Differential thermal analysis curves for the samples prepared in this work were run in an argon atmosphere heating at a rate of 3.3°C/min.

The catalytic activity of the compound oxides was tested in a horizontal 3-cm OD Pyrex glass reactor heated in a Hevi Duty Type 70 tube furnace. Temperature was measured with a Chromel-Alumel thermocouple and thermocouple potentiometer. The feed mixture contained 1.2 mole % benzene and the feed rate was 320 cc/min equivalent to 9.4 mmole benzene/hr. This is about one-tenth the space velocity used in commercial practice. Powdered oxides were tested by spreading them in a thin uniform layer in 2.3 × 16 cm trays made of 0.125-mm sheet aluminum. The trays were formed so that the space below the tray was blocked by semicircular tabs at each end of the tray.

To give a more realistic evaluation of the catalytic activity, a catalyst was prepared by coating 90 cc of 316 stainless steel Cannon-Fenske perforated saddle type column packing with 9 g of compound oxide. This was done by placing the stainless steel carrier in a large silica glass test tube (5 cm × 43 cm) which was held at an angle of about 15° to the horizontal in a muffle furnace (750°C) and rotated about its axis. At intervals, the tube was withdrawn from the furnace and held in a vertical position so that a mixture of finely powdered MoO_3 and V_2O_5 in the proportions $4MoO_3:3V_2O_5$ could be dropped directly onto the carrier. The oxide mixture was added in about 10 portions, replacing the tube in the furnace between additions and rotating it to mix the catalyst particles. The oxides fused and wet the surface of the stainless steel carrier preferentially so that a thin relatively uniform oxide coating on the carrier resulted. All but about 50 mg of the oxide adhered to the carrier; 70 cc of this catalyst was packed in a 3.0-cm Pyrex glass reactor tube to give a bed 13 cm long. The catalyst was held at 600°C in a current of air for about 3 days before testing in order to promote compound oxide formation.

The maleic anhydride formed was condensed and determined by dissolving in water and titrating with standard alkali. Benzene in the feed and effluent was measured by the ultraviolet absorption of samples of these gases.

RESULTS

Powder X-ray diffraction patterns and microscopic examination in polarized light showed that there were only three phases present in the oxides prepared by reaction of V_2O_5 and MoO_3 at 600°C, the starting materials and a phase of unknown composition. When the oxides were reacted in the ratio $3V_2O_5:4MoO_3$, these methods showed that only the unknown phase was present when reaction was complete. This required about 2 weeks at 600°C. When the vanadium:molybdenum atom ratio was greater than 3:2, V_2O_5 and the unknown phase were present together; when it was less, the unknown phase and MoO_3 were present.

The X-ray diffraction data gave no indication of the formation of solid solutions of MoO_3 in V_2O_5 since the *d* spacings measured for the V_2O_5 phase in samples where it was present were always within 0.025 Å of those of pure V_2O_5. Moreover, the *d* spacings of the unknown phase did not vary with the ratio of the oxides which reacted to form it. Therefore, it was necessary to conclude that the new phase was a compound oxide with a 3:2 atom ratio of vanadium to molybdenum.

The new phase was a shiny black material made up of small elongated crystals and aggregates. Under the polarizing microscope the smaller crystals are transparent enough to see that they show parallel extinction. Corners of the larger crystals are also transparent enough to show the same extinction.

The black color of the new phase made it seem likely that oxygen had been lost during the reaction in spite of the facts that the reaction was carried out in a sealed tube and that either V_2O_5 or MoO_3 alone could be heated at 600°C in air without oxygen loss. The extent of the loss was measured by the methods described in the experimental section. The data obtained are given in Table 1.

Table 1 shows in the first column, the number of gram atoms of Mo weighed into the sample tube in the form of MoO_3. In the second, the number of gram atoms of Mo which reacted based on a reaction in the ratio of 3V:2 Mo as required by the X-ray data. The third and fourth columns give the number of gram atoms of V weighed in as V_2O_5, and the number of gram atoms of V reacted, again based on a reaction in the ratio of 3V:2 Mo. The fifth column shows the number of gram equivalents of O collected and the sixth, the per cent of vanadium reacted which would be required to be in the V^{4+} state to account for the oxygen evolved. It is, of course, impossible to tell from these experiments whether the oxygen loss results from V^{4+} or Mo^{5+} formation during reaction. However, it should be noted

TABLE 1
ANALYTICAL DATA FOR V_3Mo_2 OXIDE

G atom Mo	G atom Mo reacted	G atom V	G atom V reacted	G eq O collected	V^{4+}/Reacted V
0.0333	0.0333	0.0666	0.0500	0.00557	0.111
0.0400	0.0400	0.0600	0.0600	0.00616	0.103
0.0444	0.0296	0.0444	0.0444	0.00468	0.105

that, even though the V_2O_5 : MoO_3 mole ratio was varied from 1:1 to 1:2, the percentage of V^{4+} or Mo^{5+} formed based on the vanadium or molybdenum reacted, assuming reaction in the ratio of 3V:2Mo, is nearly constant, probably as nearly constant as could be expected when the inherent experimental error is taken into consideration. If one assumes that one-ninth of the vanadium is in the V^{4+} state, the formula would be $Mo_6V_9O_{40}$.

Since X-ray diffraction data showed that the new phase was one of the major constituents of the active coating of vanadium–molybdenum oxide catalyst coatings, the powdered compound oxide was tested to see if it was active as a catalyst for the oxidation of benzene to maleic anhydride. Maleic anhydride was formed. Therefore, this oxide was prepared on stainless steel Cannon-Fenske saddles as a support and tested more thoroughly. The results are given in Table 2.

TABLE 2

CATALYST TEST DATA

Temp.	Mmole maleic/hr	$\frac{\text{Mole maleic}}{\text{Mole benzene}}$ (%)	Benzene consumed (%)	$\frac{\text{Mole maleic}}{\text{Mole benzene consumed}}$ (%)
445	0.63	6.7	4	—
505	2.37	25	29	—
553	3.23	34	30	—
565	3.50	37	54	68
582	1.42	15	90	17

The X-ray diffraction pattern of the used compound oxide indicated that it had been quantitatively converted to a new phase. Moreover, the X-ray diffraction data indicated that the new phase was a second major constituent of commercial vanadium–molybdenum oxide catalysts. Permanganate titration indicated that the starting oxide had been reduced and that the amount of reduction corresponded to two-thirds of the vanadium in the V^{4+} state or all the molybdenum in the Mo^{5+} state. The new phase was therefore a new 3V:2Mo compound oxide which could be formulated $Mo_4V_6O_{25}$.

Complete X-ray powder diffraction data for the original compound oxide are given in Table 3 and for the oxide obtained from it in Table 4. The data for both oxides have been indexed and show that both crystallize in the orthorhombic system. Table 5 gives the lattice constants.

TABLE 3

POWDER DIFFRACTION DATA FOR $Mo_6V_9O_{40}$

d (Å)	I/I_1	[*hkl*]	$\sin^2\theta \times 10^{-4}$ Determined	$\sin^2\theta \times 10^{-4}$ Calculated
9.667	5	100	63.5	63.5
4.833	30	200	254	254
4.557	10	210	286	286
4.118	100	022	350	350
3.782	20	122	415	414
3.558	50	202	469	468
3.299	2	103	545	546
3.228	45	300	571	572
3.155	3	041	596	598
2.696	40	312	816	820
2.642	35	133	850	852
2.551	10	150	911	914
2.513	2	331	940	932
2.415	3	400	1017	1016
2.308	3	340	1117	1116
2.215	3	421	1209	1206
2.169	2	412	1261	1264
2.133	2	252	1308	1318
2.060	60	044	1397	1400
2.011	17	144	1467	1464
1.975	5	261	1520	1528
1.943	3	324	1570	1564
1.932	20	500	1590	1588
1.905	2	423	1634	1634
1.890	10	244	1661	1654
1.861	2	054	1714	1706
1.810	18	433	1810	1804
1.784	18	450	1864	1868
1.759	15	451	1917	1920
1.744	2	263	1951	1956
1.658	15	073	2158	2148
1.632	4	081	2226	2230
1.579	20	533	2380	2376
1.566	5	444	2418	2416
1.416	10	454	2721	2722

Differential thermal analysis curves have also been obtained. For $Mo_6V_9O_{40}$ there are endothermic peaks at 581°C and 650°C, the second being the melting point. The only transition for $Mo_4V_6O_{25}$ is the melting point, 665°C. The density of $Mo_6V_9O_{40}$ is 3.86. Measurements of the relative electrical resistivity of these oxides have been made. These are given in Table 6 along with those

TABLE 4

Powder Diffraction Data for $Mo_4V_6O_{25}$

d (Å)	I/I_1	[hkl]	$\sin^2\theta \times 10^{-4}$	
			Determined	Calculated
5.997	50	200	165	165
4.092	100	002	354	356
3.520	35	012	479	487
3.358	32	020	525	524
2.994	36	400	662	661
2.706	15	003	811	801
2.673	17	103	831	842
2.429	5	402	1006	1017
2.249	3	030	1173	1179
2.044	4	004	1430	1424
1.996	7	600	1489	1487
1.930	5	413	1593	1592
1.823	5	304	1786	1796
1.806	2	503	1820	1834
1.785	3	430	1858	1840
1.771	3	314	1898	1927
1.696	2	409	2062	2085
1.681	3	040	2099	2096
1.591	2	241	2346	2350
1.566	1	504	2419	2457
1.551	4	340	2465	2468

TABLE 5

Lattice Constants of V–Mo Compound Oxide

Compound	Crystal system	a_0 (Å)	b_0 (Å)	c_0 (Å)
$Mo_6V_9O_{40}$	Orthorhombic	9.66	13.18	10.57
$Mo_4V_6O_{25}$	Orthorhombic	11.99	6.72	8.18

TABLE 6

Electrical Resistance of Oxide Samples

V_2O_5	MoO_3	$Mo_6V_9O_{40}$	$Mo_4V_6O_{25}$
2273Ω	$>10^5$Ω	25Ω	39Ω

TABLE 7

Infrared Absorption Bands of Vanadium Molybdenum Oxides

Oxide	Absorption frequencies[a] (cm⁻¹)				
V_2O_5	S 1022	B 861	B 602	B 479	S 380
MoO_3	S 994	B 862	B 578	B 495	S 372
$Mo_6V_9O_{40}$		W 770–80	B 557	W 422	
$Mo_4V_6O_{25}$	B 943	B 877	B 614	B 546	S 391

[a] B = Broad, S = Sharp, W = Weak. Run in KBr pellets.

of V_2O_5 and MoO_3 measured under the same conditions.

In addition to the data already given, infrared absorption spectra were measured as KBr pellets and Nujol mulls. The stronger absorption bands are listed below in Table 7.

As for the chemical properties of these oxides, we have already called attention to the fact that $Mo_6V_9O_{40}$ can be reduced to $Mo_4V_6O_{25}$ in a 1% benzene-air mixture at temperatures in the 500°C range. The latter compound can be reoxidized to $Mo_6V_9O_{40}$ in air. This oxide can be heated indefinitely at 600°C in air without further oxidation. Loss of MoO_3 during such heating is lower than that which would occur if MoO_3 were heated under similar conditions.

Attempts were made to prepare analogs of the compound oxides of vanadium and molybdenum described above by replacing the molybdenum with chromium or tungsten. No evidence for formation of such analogs could be found.

Discussion

Magneli and Blomberg (7) studied the vanadium pentoxide–molybdenum trioxide system. They noted "that all intermediate preparations have a grayish-black color in contrast to those of the pure oxides," and speculated that the change in color might "be connected with the existence of a state of resonance between the vanadium and molybdenum atoms." They found that a new phase was formed, a grayish-black crystal powder, which they postulated might be V_2MoO_8 or $V_2O_5{\cdot}MoO_3$, but they did not give X-ray diffraction data or analyses to support this composition. They gave no indication that there might be loss of oxygen when the two oxides are heated together. They concluded that vanadium pentoxide and molybdenum trioxide form solid solutions, citing as evidence a progressive change in unit cell dimensions from $a_0 = 11.505$ to 11.63 on increasing the mole fraction of molybdenum trioxide from zero to 0.275.

X-ray data obtained during this research show that a new phase is indeed formed when vanadium pentoxide is heated with molybdenum trioxide at 600°C and that when the two oxides are in the proportions $3V_2O_5:4MoO_3$ only the new phase, a dark crystalline material, is present.

X-ray data from this work do not show any evidence for solid solution formation in this system. The *d* spacings of vanadium pentoxide, the compound oxide and molybdenum trioxide were constant to within 0.025 Å, the limit of error of our measurements, no matter what the ratio of the oxides present in the samples. We are at a loss to explain this discrepancy between our work and that of Magneli and Blomberg, unless it is due to some difference in sample preparation.

Data given in Table 1 show that oxygen sufficient to require one-ninth the vanadium reacted to be in the V^{4+} state (or one-sixth the molybdenum to be in the Mo^{5+} state) is lost during the reaction even when the oxides are mixed in ratios other than $3V_2O_5:4MoO_3$. The oxygen loss takes place in spite of the fact that either oxide alone can be heated in air at the reaction temperature without loss of oxygen.

The facts that vanadium pentoxide and molybdenum trioxide react in the ratio $3V_2O_5:MoO_3$ and lose an amount of oxygen equivalent to reduction of one-ninth the V^{5+} to V^{4+} during reaction lead to the formula $6MoO_3{\cdot}4V_2O_5{\cdot}VO_2$ or $Mo_6V_9O_{40}$. The experimental data could just as well be explained by saying that one-sixth the molybdenum had been reduced to Mo^{5+}. We choose to assume that the vanadium is the reduced metal since V^{4+} is a well-known species in vanadium oxide chemistry, while Mo^{5+} oxide is doubtful (*10, 11*) in spite of the fact that other Mo^{5+} compounds are known.

The unit cell weight calculated from the X-ray data and the density is 3132 units. That of a unit cell containing two units $Mo_6V_9O_{40}$ would be 3348. The 6.5% difference is probably due to a low density value caused by inability to completely fill voids in the sample during the pycnometric density determination. Unfortunately, single crystals of $Mo_6V_9O_{40}$ and $Mo_4V_6O_{25}$ suitable for X-ray diffraction studies could not be obtained from any of our preparations so that the space groups could not be assigned. However, orthorhombic unit cells containing 1 or 2 molecules per unit cell are known.

The formula for the more reduced 3V:2Mo oxide in which permanganate titration indicates sufficient reduction to require two-thirds of the vanadium as V^{4+} or all the molybdenum as Mo^{5+} can also be written assuming either V^{4+} or Mo^{5+}. For the same reason as noted above, we prefer the formulation $4MoO_3{\cdot}4V_2O_5{\cdot}4V_2O_4$ or $Mo_4V_6O_{25}$.

As can be seen from Table 3, unusually good agreement between calculated and measured values of $\sin^2 \theta$ was obtained when the lattice constants for $Mo_6V_9O_{40}$ were calculated. The data of Table 4 for $Mo_4V_6O_{25}$ show that the agreement in this case, while satisfactory, was not as precise. This is probably caused by the fact that the latter compound was not as highly crystalline as the former and gave somewhat less sharp diffraction peaks which could not be measured as accurately.

Inspection of the data given in Table 6 shows that the compound oxides have resistivities two orders of magnitude lower than that of pure vanadium pentoxide and four orders of magnitude or more lower than that of molybdenum trioxide. It is somewhat surprising to note that the more reduced of the compound oxides, $Mo_4V_6O_{25}$, has a higher resistivity than the more oxidized $Mo_6V_9O_{40}$.

The infrared absorption data for $Mo_6V_9O_{40}$ and $Mo_4V_6O_{25}$ given in Table 7 show a similar anomaly. The more oxidized of the compound oxides, $Mo_6V_9O_{40}$, has only three comparatively weak absorption bands while $Mo_4V_6O_{25}$ has five, all of which are stronger. This is the reverse of what would be expected since the more reduced compound should have more metallic character and more general absorption. However, it should be noted that this corresponds with the indication of the electrical resistivity measurements, where as was pointed out above, the more reduced oxide has higher resistivity.

Table 8 gives the X-ray diffraction data for a typical commercial vanadium–molybdenum oxide catalyst for oxidizing benzene

TABLE 8
X-RAY POWDER DIFFRACTION DATA[a]

		Vanadium-molybdenum oxides			
Catalyst coating		$Mo_6V_9O_{40}$		$Mo_4V_6O_{25}$	
d (Å)	I/I_1[b]	d (Å)	I/I_1	d (Å)	I/I_1
9.71	2	9.68	5		
5.95	25			5.997	50
4.818	15	4.833	30		
4.115	100	4.118	100		
4.090	50			4.092	100
3.765	10	3.782	20		
3.551	17	3.558	50		
3.531	20			3.520	35
3.422	20[c]				
3.366	15			3.358	32
3.230	25	3.228	45		
3.160	3	3.155	3		
3.022	27			2.994	36
2.910	15[c]				
2.685	60	2.696	40	2.706	15
2.655	10			2.673	17
2.635	15	2.642	35		
2.547	5	2.551	10		
2.415	3			2.429	5
2.290	3	2.308	3		
2.083	35	2.060	60		
1.992	4			1.996	7
1.924	15	1.932	20	1.930	5
1.886	5	1.890	10		
1.826	3			1.823	5
1.548	2			1.551	4

[a] Filtered Cu $K\alpha$ radiation; d = interplanar spacing.

[b] I/I_1 = relative peak intensity.

[c] Broad peaks, not identified.

to maleic anhydride along with data for $Mo_6V_9O_{40}$ and $Mo_4V_6O_{25}$. It can be seen that the two compound oxides are the major components of the commercial catalyst accounting for all its diffraction peaks, except the two broad unidentified ones. In some catalyst samples, V_2O_5 can also be identified. This does not rule out the presence of small amounts of other phases which are below the limit of detection by X-ray diffraction methods, particularly in the case of vanadium oxide–molybdenum oxide catalysts containing trace amounts of additives. It should be noted that $V_{12}O_{26}$ found in vanadium oxide catalysts used to produce phthalic anhydride from naphthalene, is not present in the vanadium oxide–molybdenum oxide maleic catalysts examined here.

The data in Table 2 indicate that the two new oxides we have prepared are catalytically active. However, a catalyst in which these are the only constituents is not a particularly good one for the commercial production of maleic anhydride from benzene because it must be operated at lower space velocity and higher temperatures to give equivalent yield and conversion. This might be because the coatings were deliberately prepared to be as highly crystalline as possible. It might also be that minor additives used in commercial catalysts are responsible for their improved performance or to a combination of factors.

Ioffe and his co-workers (*9*) have conducted an investigation of the phase composition of mixed vanadium oxide–molybdenum oxide catalysts used for the oxidation of aromatic hydrocarbons. They indicate that they have found X-ray diffraction evidence for the existence of two vanadium-molybdenum-oxygen phases, one formed by heating their catalyst to 400°C and designated $(VMoO)_{400}$, the second formed on heating to 550°C and designated $(VMoO)_{550}$. They assumed, on the basis of Magneli and Blomberg's (*7*) work and of that by Tarama (*8*), that these were interstitial compounds. Unfortunately, they give their X-ray diffraction data only in the form of bar graphs on such a small scale that they cannot be read accurately. However, it appears that their $(VMoO)_{400}$ might contain our $Mo_4V_6O_{25}$ and their $(VMoO)_{550}$, our $Mo_6V_9O_{40}$. They prepared their catalyst by mixing aqueous solutions of "vanadium oxalate" and ammonium molybdate in the desired proportions, evaporating the mixture to dryness and heating to 400°C in a muffle furnace in some cases or to 550°C in others. It is almost certain that a large part of the vanadium in a solution containing an equivalent amount of oxalate ion would be reduced. Thus, the product they obtained on heating to 400°C could very easily contain the more reduced of the two oxides prepared in pure form in this work, $Mo_4V_6O_{25}$. Heating at 600° in air has been shown here to convert this oxide to the more oxidized of the two oxides prepared in pure form in this work. Thus, their $(VMoO)_{550}$ might well contain our $Mo_6V_9O_{40}$.

Butler and Weston (*12*) have carried out another recent investigation of mixed vanadium–molybdenum oxide catalysts. It was their purpose to change the semiconducting properties of vanadium pentoxide catalysts by "doping" them with altervalent ions and studying the effect this had on the kinetics of the oxidation of benzene over the resulting catalysts. They chose molybdenum as the hexavalent ion and assumed, on the basis of the work by Magneli and Blomberg (*7*), that their catalysts were solid solutions of molybdenum trioxide in vanadium pentoxide. They prepared their catalysts by heating oxide mixtures containing 8.6 and 16.0 mole % of molybdenum trioxide to 620°C. Under these conditions their catalyst would have contained vanadium pentoxide plus $Mo_6V_9O_{40}$ and/or $Mo_4V_6O_{25}$ rather than being a solid solution of molybdenum trioxide in vanadium pentoxide.

In conclusion, it can be stated that two new vanadium–molybdenum compound oxides have been prepared and characterized. Both are present in all commercial vanadium–molybdenum oxide catalysts examined during this work. In some cases vanadium pentoxide is also present. X-ray diffraction data do not permit identification of any other components than these three in this type of catalyst. $V_{12}O_{26}$ is formed by reduction when pure vanadium pentoxide catalysts are used, but has not been found in the mixed vanadium–molybdenum oxide catalysts.

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