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Metal Telluromolybdates of the Type MTeMoO$_6$

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The solid state reactions of MMoO$_4$ ($M = Mg^{2+}$, Fe^{2+}, and Ni^{2+}) and orthorhombic TeO$_2$ were investigated. A new metal telluromolybdate MgTeMoO$_6$ was obtained in the case of Mg; its structure belongs to the orthorhombic system with unit-cell dimensions $a = 5.262$ Å, $b = 5.028$ Å, $c = 8.880$ Å. $Fe_2(MoO_4)_3$ and a new compound were formed in the case of Fe. The new compound is made up with Fe^{3+} ions and its chemical formula cannot be recognized as FeTeMoO$_6$. In the case of Ni a complex reaction mixture is obtained. An explanation is given of the ability of M^{2+} ions to form the metal telluromolybdates. The catalytic properties of MgTeMoO$_6$ are discussed and compared to those of the other metal telluromolybdates.

Introduction

The synthesis of new phases such as CdTeMoO$_6$ (*1*), CoTeMoO$_6$ (*2*), MnTeMoO$_6$ (*3*), and ZnTeMoO$_6$ (*4*) by solid state reaction at 500°C of MMoO$_4$ and orthorhombic TeO$_2$ was recently reported. The X-ray powder patterns were indexed on the basis of a tetragonal unit cell in the case of CdTeMoO$_6$ (*5*) and orthorhombic unit cells for CoTeMoO$_6$, MnTeMoO$_6$, and ZnTeMoO$_6$ (*6*). Further, Sloczynski and Sliwa have reported the synthesis of NiTeMoO$_6$ (*7*); however, definitive evidence for the formation of this compound is lacking. Attempts to obtain Ca-, Ba-, and Pb-telluromolybdate from the corresponding molybdate and orthorhombic TeO$_2$ were unsuccessful. The solid mixtures did not undergo any reaction up to temperatures as high as 650°C (*4*).

The present study was undertaken to explore the possibility that new metal telluromolydates could be formed also in the case of Mg^{2+} and Fe^{2+} ions and to further investigate the solid state reaction of NiMoO$_4$ and orthorhombic TeO$_2$. The final purpose was to offer a comprehensive picture of the ability of the different M^{2+} ions to form the corresponding metal telluromolybdates.

The investigation of these new phases is of industrial and scientific importance for the following reasons:

(i) Metal telluromolybdates MTeMoO$_6$ represent a new class of selective catalysts for the allylic oxidation and ammoxidation of olefins (*8*, *9*).

(ii) Multicomponent oxide systems based on Mo, small amounts of Te, and other elements are well-known commercial catalysts for the above reactions (*10*). Understanding of phase composition in M–Te–

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Mo–O systems and its relation to the activity and selectivity in commercial catalysts is therefore of great importance.

Experimental

$FeMoO_4$, $MgMoO_4$, and $NiMoO_4$ were prepared by evaporating a solution of the metal nitrate and ammonium molybdate. Drying overnight at 110°C and calcination at 500°C for 12 hr followed. A protective N_2 atmosphere was necessary to prevent oxidation of Fe^{2+} to Fe^{3+}.

The solid state reactions of the molybdates and orthorhombic TeO_2 were performed by heating in air intimate mixtures having a Mo/Te molar ratio of 1 at different temperatures. In the case of $FeMoO_4$ two different preparative techniques were used. By the first method, the mixture was sealed in an evacuated tube and then heated. In the second method the reaction was performed under N_2 atmosphere. All reactants were of reagent-grade quality.

The products of solid state reactions were characterized by infrared (ir) and Raman spectroscopies and X-ray diffraction. Infrared spectra were obtained on KBr disks using a Perkin–Elmer 457 apparatus. Raman spectra were measured on a Cary 83 laser–Raman spectrophotometer (4880-Å excitation). X-Ray powder patterns were recorded at 25°C using a Philips PW 1050 counter diffractometer with Cu$K\alpha$ radiation (λ = 1.5418 Å). The cell dimensions were refined by a least-squares method.

Differential thermal analysis (DTA) experiments were performed on a TG2000 Mettler analyzer. The heating rate was 5°C/min and a protective N_2 atmosphere was always employed.

Results and Discussion

(a) Mg–Te–Mo–O System

The solid state reaction of $MgMoO_4$ and orthorhombic TeO_2 at 500°C leads to the formation of a new compound $MgTeMoO_6$. The X-ray powder pattern of the solid product was indexed on the basis of an orthorhombic unit cell. The observed spacings and relative intensities are listed in Table I. Cell parameters are as follows: a = 5.262(1) Å; b = 5.028(1) Å; c = 8.880(3) Å; V = 234.94 Å^3. The observed systematic

TABLE I

X-RAY POWDER PATTERN OF $MgTeMoO_6$

$h\ k\ l$	d_{calc}	d_{obs}	I/I_0
0 0 2	4.444	4.45	61
0 1 1	4.376	4.37	6
1 1 0	3.635	3.64	95
1 0 2	3.394	3.39	15
1 1 1	3.364	3.37	19
0 1 2	3.328	3.33	25
0 0 3	2.960	2.965	3
1 1 2	2.813	2.817	100
2 0 0	2.631	2.630	15
1 0 3	2.580	2.579	5
0 1 3	2.551	2.549	6
2 0 1	2.520	2.512	13
0 2 0	2.514		
1 1 3	2.295	2.295	9
2 0 2	2.263	2.263	16
0 0 4	2.220	2.220	5
0 2 2	2.188	2.188	14
2 1 2	2.064	2.063	4
1 0 4	2.046	2.046	4
2 0 3	1.967	1.968	4
0 2 3	1.916	1.916	5
1 1 4	1.895	1.895	7
2 2 0	1.818	1.818	21
1 2 3	1.801	1.801	7
2 0 4	1.697	1.697	5
2 2 2	1.683	1.682	14
1 0 5	1.682		
0 2 4	1.664	1.665	5
3 0 2	1.630	1.629	3
2 1 4	1.608	1.607	4
1 1 5	1.596	1.597	8
1 3 0	1.597		
1 2 4	1.587	1.587	7
1 3 1	1.572	1.573	3
3 1 2	1.552	1.552	14
2 2 3	1.550		
3 0 3	1.504	1.503	13
1 3 2	1.503		

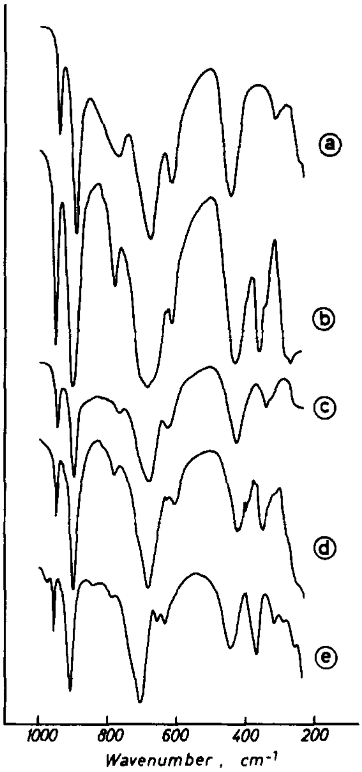

FIG. 1. Infrared spectra of $CdTeMoO_6$ (a), $CoTeMoO_6$ (b), $MnTeMoO_6$ (c), $ZnTeMoO_6$ (d), and $MgTeMoO_6$ (e).

extinctions ($h = 2n + 1$ for $h00, k = 2n + 1$ for $0k0$) limited the choice of the space group to $P2_12_12$. The calculated density, assuming $z = 2$, is $D_x = 4.860(3)$ g cm^{-3}, which compares well with the pycnometric density $D_m = 4.79 \pm 0.10$ g cm^{-3}.

An endothermic DTA peak, attributable to the melting of $MgTeMoO_6$ with decomposition, has been observed at 660°C. The ir and Raman spectra of the new phase were also collected; they are shown in Figs. 1 and 2 together with those of other compounds.

(b) Fe–Te–Mo–O System

The solid state reaction of $FeMoO_4$ and orthorhombic TeO_2 occurs at temperatures higher than 550°C. The X-ray powder pattern of the product obtained at 560°C from

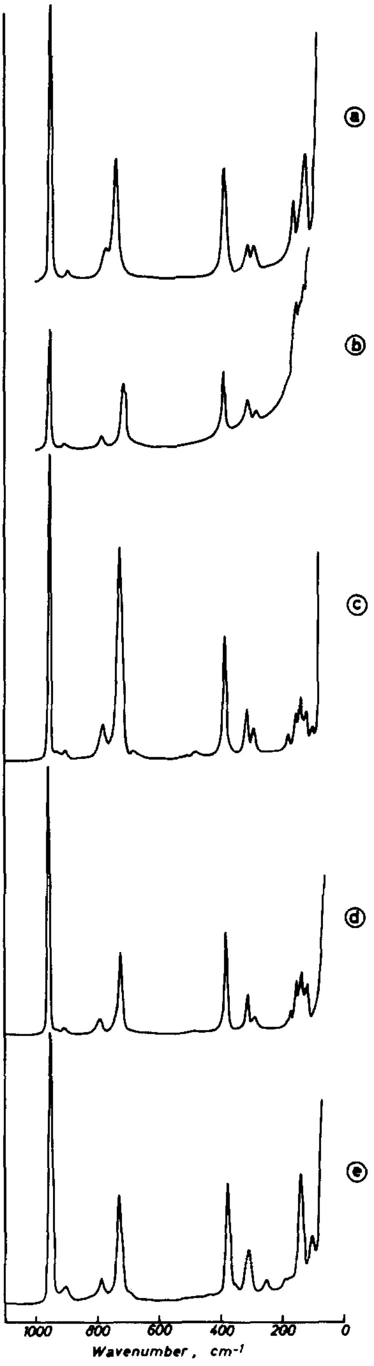

FIG. 2. Raman spectra of $CdTeMoO_6$ (a), $CoTeMoO_6$ (b), $MnTeMoO_6$ (c), $ZnTeMoO_6$ (d), and $MgTeMoO_6$ (e).

mixture sealed in an evacuated tube is given in Table II. A similar pattern was obtained when operating under N_2. The peaks at d = 4.34, 4.08, 3.91, 3.87, 3.46, 3.25, and 2.628 Å can be attributed to $Fe_2(MoO_4)_3$. All the other peaks can be indexed on the basis of an orthorhombic unit cell. Cell parameters are as follows: a = 6.132(3) Å; b = 7.610(3) Å; c = 4.395(2) Å; V = 205.10 Å^3. An endothermic DTA peak, attributable to the congruent melting of the indexed compound, has been observed at 670°C.

TABLE II

X-RAY POWDER DATA FOR $FeMoO_4 + TeO_2$

d_{obs}	d_{calc}	I/I_0	$h\ k\ l$
7.61	7.599	7	0 1 0
4.78	4.775	1	1 1 0
4.39	4.389	10	0 0 1
4.34[a]		3	
4.08[a]		5	
3.91[a]		6	
3.87[a]		10	
3.803	3.806 3.805	13	0 1 1 0 2 0
3.573	3.572	100	1 0 1
3.46[a]		7	
3.25[a]		5	
3.234	3.234 3.233	11	1 1 1 1 2 0
3.067	3.066	6	2 0 0
2.876	2.877	14	0 2 1
2.841	2.844	5	2 1 0
2.693	2.694	3	1 2 1
2.628[a]		4	
2.536	2.537	16	0 3 0
2.514	2.515	20	2 0 1
2.389	2.388 2.388	4	2 1 1 2 2 0
2.344	2.344	5	1 3 0
2.199	2.197 2.197	3	0 0 2 0 3 1
2.112	2.111	4	0 1 2
2.067	2.068 2.069	3	1 3 1 1 0 2
1.955	1.955	5	2 3 0
1.854	1.853	10	3 0 1
1.786	1.786 1.786	7	2 3 1 2 0 2
1.739	1.739	7	2 1 2
1.679	1.679	4	1 4 1
1.603	1.603	4	1 3 2

[a] Attributable to $Fe_2(MoO_4)_3$.

The extra peaks attributable to $Fe_2(MoO_4)_3$ appeared with much higher intensities in preparations performed at lower temperatures (500–520°C), suggesting thus that $Fe_2\ (MoO_4)_3$ is an intermediate reaction product. The direct reaction of $Fe_2(MoO_4)_3$ and TeO_2 was confirmed to lead to the new compound.

It is therefore proved that the solid state reaction of $FeMoO_4$ and orthorhombic TeO_2 results in the formation of $Fe_2\ MoO_4)_3$ and of a new compound which is made up with Fe^{3+} ions. The reaction is complicated by the oxidation of Fe^{2+} to Fe^{3+} even in the absence of oxygen. Under these conditions the above oxidation may result from internal redox processes involving Fe and Te (or Mo) ions. This oxidation does not permit the synthesis of $FeTeMoO_6$.

(c) Ni–Te–Mo–O System

The solid state reaction of $NiMoO_4$ and orthorhombic TeO_2 was studied in a wide temperature range (500–650°C). The X-ray powder pattern of the solid product obtained at 550°C is given in Table III. Attempts to index this pattern were unsuccessful. Very similar patterns were observed at the other investigated temperatures. DTA analysis did not show any peak up to 750°C: only an appreciable drift of the baseline occurred in the temperature range 500–750°C.

These results do not offer any definitive indication that a new compound $NiTeMoO_6$ was formed. On the contrary there is evidence for the formation of a complex reaction mixture.

(d) M–Te–Mo–O Systems vs MTeMoO$_6$ Telluromolybdates

The data so far obtained and those already published in the literature indicate that the solid state reaction of $MMoO_4$ and

TABLE III

X-RAY POWDER DATA FOR $NiMoO_4 + TeO_2$

d_{obs}	I/I_0
5.79	19
4.64	27
4.38	12
3.27	100
3.18	23
2.984	27
2.887	77
2.739	17
2.650	27
2.496	10
2.408	12
2.303	6
2.072	27
1.989	12
1.768	12
1.706	8

orthorhombic TeO_2 gives rise to the formation of the corresponding telluromolybdates in the case of Mg, Co, Zn, Mn, and Cd. On the other hand $CaMoO_4$, $BaMoO_4$, and $PdMoO_4$ do not undergo any reaction at all. A complex mixture of compounds is obtained in the case of $NiMoO_4$ while the solid state reaction of $FeMoO_4$ and orthorhombic TeO_2 is complicated by internal redox processes.

In Table IV we summarize the unit-cell dimensions and the melting points of the different telluromolybdates. All such compounds exhibited very similar X-ray powder patterns with respect to *d* values and relative intensities. This results in isomorphous or nearly isomorphous compounds and in similar unit-cell dimensions.

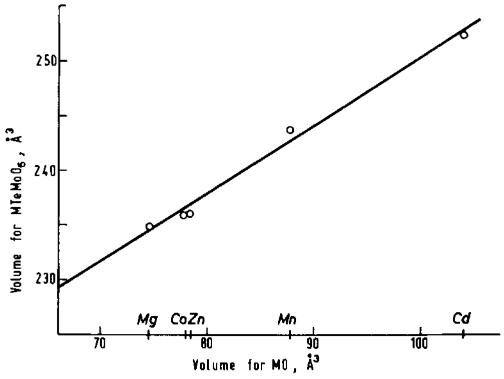

FIG. 3. Cell volumes of MTeMoO$_6$ vs cell volumes of MO rock-salt compounds.

In Fig. 3 the cell volumes of the MTeMoO$_6$ telluromolybdates are plotted against the cell volume of the rock-salt MO compound. Data for the rock-salt cell volumes were taken from Ref. (*11*), except the value for ZnO which was obtained from Ref. (*12*). The trend is quite consistent and the figure suggests that the volume of the rock-salt cell is critical for the synthesis of the MTeMoO$_6$ telluromolybdates. Indeed Ca, Ba, and Pb show rock-salt cells much larger than that of Cd, while the volume of NiO is smaller than that of MgO.

Figure 3 suggests that the structure of MTeMoO$_6$ telluromolybdates may be regarded as made up of Mo, Te, and O atoms occupying definite positions with certain

TABLE IV

CRYSTAL AND DTA DATA FOR MTeMoO$_6$ TELLUROMOLYBDATES

Compound	*a* (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)	DTA peak temperature (°C)
$MgTeMoO_6$	5.262	5.028	8.880	234.94	660
$CoTeMoO_6$	5.262	5.062	8.857	235.93	680
$ZnTeMoO_6$	5.255	5.044	8.909	236.14	660
$MnTeMoO_6$	5.294	5.139	8.960	243.75	710
$CdTeMoO_6$	5.279		9.056	253.37	760

sites filled by M cations. The M cations are coordinated to oxygen and the structure appears to be stable only for M–O bond lengths within a proper range.

Although all the MTeMoO$_6$ telluromolybdates display strong structural analogies and similar unit-cell dimensions, a higher symmetry is acheived in CdTeMoO$_6$. This compound has a tetragonal unit cell as opposed to orthorhombic unit cells for the other compounds.

Infrared and Raman spectra, which are shown in Figs. 1 and 2, offer additional evidence for a trend for lower symmetry.

Although assignment of the ir and Raman frequencies of MTeMoO$_6$ telluromolybdates is difficult since the structures of these compounds are unknown, some information can still be obtained by comparison of the spectra. Differences in the Raman spectra concern the line present at 765 cm^{-1} in CdTeMoO$_6$, which is shifted to 780 cm^{-1} in the other telluromolybdates, and a change in the ratio of the intensities of the lines at 400 and 380 cm^{-1} by going from Cd to the other cations. The line at 380 cm^{-1} is shifted to 350 cm^{-1} in MgTeMoO$_6$. Concerning the ir spectra additional absorptions at 650, 840, and 970 cm^{-1} become clear for MgTeMoO$_6$.

The more rich general pattern of the ir spectrum of MgTeMoO$_6$ is consistent with a greater complexity of the Te–O and Mo–O bond geometries and thus with a lower structural order of this compound. In addition, the differences in the Raman spectra of Cd-telluromolybdate and of the other metal telluromolybdates are consistent with differences in space lattices (i.e., tetragonal vs orthorhombic unit cells).

Another trend can be observed within the series and it concerns a decrease in the melting point by going from Cd to Mg. This means that there is greater difficulty in retaining the MTeMoO$_6$ structure and it can finally be related to a lower structural order.

(e) Catalytic Properties of MeTeMoO$_6$ Telluromolybdates

Previous investigation showed comparable catalytic behavior for Cd-, Co-, Mn-, and Zn-telluromolybdates (*8, 9*). Selectivities to butadiene, acrolein, and acrylonitrile of 80–90% were observed at conversion levels of 60–80% in the oxidation of butene and in the oxidation and ammoxidation of propylene.

In the case of MgTeMoO$_6$, only the propylene oxidation was briefly examined. Again selectivities higher than 90% were obtained with consumption of propylene as high as 30%. The temperature required to obtain this conversion was 530°C, i.e., much higher than those reported in Ref. (*8*) for the same conversion level. However, the surface area of MgTeMoO$_6$ was smaller, due to prolonged calcination (24 hr at 550°C), and the GHSV value was higher.

Comparison of the activity of MgTeMoO$_6$ with those of the other telluromolybdates can be performed in terms of specific rate constants. Under assumption of isothermal plug flow conditions and first-order kinetics we have:

$$k = \frac{1}{\theta S}[-\ln(1-x)],$$

where k = specific rate constant; S = surface area; θ = contact time; x = conversion of propylene.

Calculations at 400°C give:

$$k_{\mathrm{MgTeMoO_6}}/k_{M\mathrm{TeMoO_6}} = \frac{1}{\theta_1 S_1}[-\ln(1-x_1)]/\frac{1}{\theta_2 S_2}[-\ln(1-x_2)] = 0.78 \div 0.96,$$

based on the data $x_1 = 0.025$, $S_1 = 0.4$ m^2/g, $1/\theta_1 = 3500$ hr^{-1}, and $x_2 = 0.25 \div 0.3$, $S_2 = 3$ m^2/g, $1/\theta_2 = 2400$ hr^{-1}. Calculations were limited to this temperature where the hypothesis of isothermality can still be retained for $M\text{TeMoO}_6$ and the conversion for MgTeMoO_6 is of significance.

The results indicate that MgTeMoO_6 displays a specific activity comparable to those of the other metal telluromolybdates.

Conclusions

The ability of the different M^{2+} ions to form the metal telluromolybdates has been found to be related to the volume cell of the rock-salt MO compound and thus the M–O bond length. Accordingly $M\text{TeMoO}_6$ telluromolybdates could be formed only in the case of Mg, Co, Zn, Mn, and Cd cations. Within this class of compounds a trend for lower structural order exists.

It has been confirmed also in the case of MgTeMoO_6 that metal telluromolybdates represent a new class of highly selective catalysts of comparable activity for the allylic oxidation of olefins. As already pointed out elsewhere (*8*) their performances are quite noticeable and compare well with those reported for known effective catalysts such as bismuth molybdates.

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