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Solid State Reactions to $CdTeMoO_6$ and Its Structural Characterization

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$CdTeMoO_6$ has been obtained by solid state reactions of $CdMoO_4$ with orth. TeO_2 at 425°C, with tetr. TeO_2 at 470°C, and with H_6TeO_6 at 490°C. Its crystal structure belongs to the tetragonal system (space group $P4/n$ or $P4/nmm$) with unit cell dimensions $a = 5.279(2)$ Å, $c = 9.056(2)$ Å. The specificity of this compound in the allylic oxidation reactions should be strictly related to its structural features, among which the presence of *cis* MoO_2 groups could be very important.

Introduction

During a phase study of the Cd–Te–Mo–O system, the formation of the compound $CdTeMoO_6$, by solid state reaction of $CdMoO_4$ and orth. TeO_2 at 500°C, has been observed (*1*). This compound proved to be highly specific for the oxidation of butene to butadiene (*2*) and of propylene to acrolein (*3*).

Commercial catalysts containing Cd, Te, Mo, and O appear from the patent literature to be very effective for the selective allylic oxidation of olefins (*4*). They are usually prepared following a coprecipitation procedure starting from the corresponding soluble salts. In this case one would expect to obtain a precipitate which contains, among other compounds, $CdMoO_4$ and telluric acid H_6TeO_6, which therefore are involved as reactants in the subsequent calcination step at high temperatures. Tetr. TeO_2 is also a possible reactant since H_6TeO_6 easily transforms to TeO_3, which in turn gives tetr. TeO_2 at about 430°C (*5*).

From these considerations we thought it interesting to study the solid state reactions of $CdMoO_4$ with H_6TeO_6 and with tetr. TeO_2, besides closely examining the reaction with orth. TeO_2.

We also report further information about the crystal structure of $CdTeMoO_6$, since knowledge of the structural properties may be very important in explaining the specificity of this compound in allylic oxidation reactions.

Experimental

$CdMoO_4$ was prepared according to Ref. (*6*) and dried at 110°C for 2 hr. Orth. TeO_2 and H_6TeO_6 were Merck RP reactants. Tetr. TeO_2 was obtained by heating H_6TeO_6 at 500°C for 3 hr.

The solid state reactions of $CdMoO_4$ with orth. TeO_2, H_6TeO_6, and tetr. TeO_2 were studied by performing thermogravimetric (TG) and differential thermal analyses (DTA) on mixtures with Mo/Te molar ratios 1/1, up to 550°C. A Netzsch Gerätebau GmbH apparatus (Model 429) was employed with a heating rate of 10°C/min. The solid products were characterized by infrared (ir) and Raman

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(R) spectroscopy. 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).

Crystals of $CdTeMoO_6$ were obtained by heating an intimate mixture of stoichiometric amounts of $CdMoO_4$ and orth. TeO_2, followed by slow cooling from below the melting point (760°C). The X-ray powder pattern was measured on a Philips PW 1050 counter diffractometer using Cu$K\alpha$ radiation (λ = 1.5418 Å).

Results and Discussion

(a) *Solid State Reactions*

The TG and DTA curves for each of the mixtures investigated are given in Fig. 1.

The $CdMoO_4$–orth. TeO_2 system exhibits only exothermic peak at 425°C without any weight loss; this thermal effect is due to the formation of the compound $CdTeMoO_6$, as confirmed by ir and R analyses. The same occurs for the $CdMoO_4$–tetr. TeO_2 mixture at 470°C. The DTA curve of the $CdMoO_4$–H_6TeO_6 mixture shows an endothermic effect at 140°C with a weight loss of about 10%, corresponding to the complete dehydration of H_6TeO_6. A series of effects above 300°C that finally bring to tetr. TeO_2 (*5*), and an exothermic effect at 490°C are also shown. This last effect is associated with the formation of $CdTeMoO_6$, as confirmed by ir and R analyses.

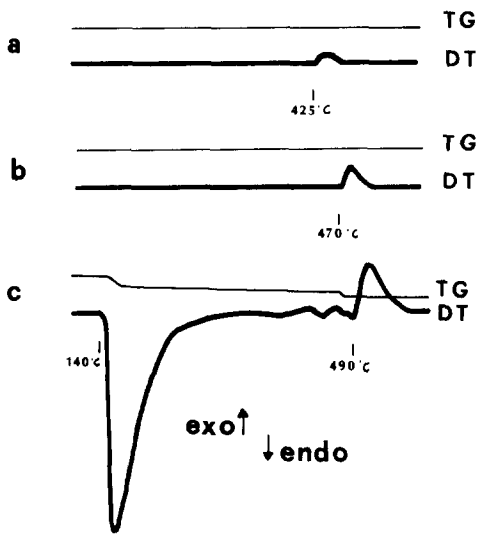

FIG. 1. Thermogravimetric (—, TG) and differential thermal (—, DT) curves for $CdMoO_4$–orth. TeO_2 (a), $CdMoO_4$–tetr. TeO_2 (b), and $CdMoO_4$–H_6TeO_6 (c) mixtures.

(b) *Catalytic Activity*

As previously reported, $CdTeMoO_6$ proved to be specific for the oxidation of butene to butadiene and of propylene to acrolein. Further results from a study of its catalytic activity showed that in both cases selectivities higher than 90% were also retained at conversion levels which approach 80–90%.

(c) *Structural Characterization*

The X-ray powder diffraction pattern of the title compound was indexed on the basis of a tetragonal unit cell, and is shown in Table I. Cell parameters, refined using a least-squares method, are as follows:

$a = 5.279(2)$ Å; $c = 9.056(2)$ Å; $V = 252.37$ Å^3.

The calculated density, assuming two formula units per unit cell, is $D_x = 5.682$ g cm^{-3}, while the pycnometric density is $D_m = 5.59$ g cm^{-3}.

Single crystal precession photographs showed systematic absences only of *hko* reflexions for $h + k = 2n + 1$, thus indicating the possible space groups $P4/n$ or $P4/nmm$. The crystals exhibit a plate-like shape with the short dimension parallel to the c crystallographic axis.

Although there are some analogies between the crystal structures of $CdMoO_4$ (which has a scheelite-type structure with tetragonal space group $I4_1/a$ (*7*)) and $CdTeMoO_6$, since both unit cells belong to the tetragonal system and have comparable a axis lengths, the different symmetry space groups require different arrangements of the structural units in the unit cells. Indeed the shape of the crystals suggests,

TABLE I

X-RAY POWDER PATTERN OF $CdTeMoO_6$

$h\,k\,l$	d_{calc}	d_{obs}	I/I_0
0 0 1	9.055	9.034	25
0 0 2	4.528	4.522	12
1 1 0	3.733	3.729	16
1 1 1	3.451	3.448	48
0 0 3	3.018	3.015	18
1 1 2	2.880	2.880	100
2 0 0	2.640	2.641	23
1 0 3	2.620	2.620	11
2 0 1	2.534	2.532	4
1 1 3	2.347	2.348	4
2 1 1	2.284	2.284	5
0 0 4	2.264	2.263	11
2 1 2	2.093	2.094	3
1 0 4	2.081	2.080	3
2 0 3	1.987	1.988	22
2 2 0	1.866	1.867	18
2 2 1	1.828	1.829	2
2 2 2	1.726	1.726	4
2 0 4	1.718	1.720	11
1 0 5	1.713	1.714	11
3 1 1	1.642	1.643	7
1 1 5	1.630	1.630	11
2 2 3	1.588	1.588	5
3 1 2	1.566	1.567	19

for $CdTeMoO_6$, a layer structure, which does not occur in the scheelite-type (pseudocubic) structure of $CdMoO_4$.

Further, information on the structural features of $CdTeMoO_6$ is given by ir and R spectra. Both showed bands at 945, 890, and 380 cm^{-1} which have been interpreted as $\nu^{as}(MoO_2)$, $\nu^{s}(MoO_2)$, and $\delta(MoO_2)$ from *cis* MoO_2 groups (*1*). The occurrence of these bands at frequencies higher than in $CdMoO_4$, indicates a shortening of Mo–O bonds which assume a higher double bond character.

Groups of this type, by providing two contiguous points for the removal of hydrogen atoms, could be very effective in allylic oxidations, according to the role of Mo=O species in these reactions (*8*).

Conclusion

It has been found that $CdTeMoO_6$ can be formed by solid state reaction of $CdMoO_4$ either with TeO_2 (both orth. and tetr.) or with H_6TeO_6. This indicates that the title compound is probably present in commercial oxide catalysts containing Cd, Te, Mo, and other elements which are prepared by coprecipitation from corresponding soluble salts. Actually in this case the precipitate is expected to contain, among other phases, $CdMoO_4$ and telluric acid.

The structural features of $CdTeMoO_6$ discussed here are believed to play an important role in determining its noticeable catalytic behavior.

Other compounds with the same chemical compositions as $CoTeMoO_6$ (*9*), $MnTeMoO_6$ (*10*), and $ZnTeMoO_6$ (*11*) have been synthesized; they also proved to be active and extremely selective in the oxidation of butene and propylene (*12*). Actually, the structures of these compounds are expected to be very similar to that of $CdTeMoO_6$ since all the X-ray diffraction patterns show analogies for both position and relative intensity of the peaks (*11*), and the ir and R spectra exhibit very close general patterns. In particular the bands which in the case of $CdTeMoO_6$ have been assigned to vibrational modes from *cis* MoO_2 groups are also present in the ir and R spectra of $CoTeMoO_6$, $MnTeMoO_6$, and $ZnTeMoO_6$, nearly at the same frequencies (*12*).

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