CdTeMoO₆, CoTeMoO₆, MnTeMoO₆, and ZnTeMoO₆: A New Class of Selective Catalysts for Allylic Oxidation of Butene and Propylene

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CdTeMoO₆, CoTeMoO₆, MnTeMoO₆, and ZnTeMoO₆ represent a new class of selective catalysts for the allylic oxidation of butene to butadiene and propylene to acrolein. These catalysts are highly specific for butadiene and acrolein even at high conversions. Infrared, Raman, and X-ray analyses clearly show that each catalyst is a single chemical compound. Their similar catalytic behavior is related to their analogous structural properties. It is suggested that the active centers involved in the allylic oxidation are either cis-MoO₂ groups with high Mo=O character or sites directly connected with tellurium. Probably the third metal plays only a minor role, if any, during the olefin oxidation.

INTRODUCTION

Multicomponent oxide systems containing molybdenum as a basic component, small amounts of Te, and other elements are well-known commercial catalysts highly active and selective in the oxidation of olefins. An understanding of phase composition and its relation to the activity and selectivity of these systems is therefore of industrial and scientific importance.

New compounds with fixed chemical composition such as MeTeMoO₆ were observed in the Me–Te–Mo–O systems (1–4) and gave rise to the present investigation.

This paper reports a study which was undertaken to explore the behavior of these new phases (CdTeMoO₆, CoTeMoO₆, and ZnTeMoO₆) in the oxidation of butene and propylene. The knowledge of their catalytic behavior is an important point of reference in the discussion of the performances of the corresponding Me–Te–Mo–O systems and for a further clarification of the role of Te in allylic oxidation reactions.

METHODS

The catalysts used in these studies were obtained by solid state reaction of the molybdate with orthorombic TeO₂ at 500°C (2 hr). The preparations of CdMoO₄ (5), CoMoO₄ (5), and MnMoO₄ (6) have already been reported elsewhere. ZnMoO₄ was precipitated from an ammonium molybdate solution (heated at 80°C and brought to pH 5.5 with diluted ammonia) by mixing under vigorous stirring with a zinc nitrate solution to give a final pH 4.3 and a zinc to molybdenum atomic ratio of 1. The precipitate was aged for 45 min inside the mother liquors at 80°C, filtered, and dried overnight.

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The granules of the different catalysts were obtained by pressing the calcined powders at 300 kg cm^{-2} for 5 min, followed by grinding to the desired mesh. The surface area of these catalysts is a few square meters per gram (about 3 m^2 g^{-1}). Over a period of 12 hr of use no sign of deactivation was observed.

Different testing systems were employed. The oxidation of butene was carried out in a fixed-bed reactor, in Pyrex glass, of 14.2-mm i.d. with a concentric thermocouple and using a 100-ml min^{-1} gas flow of 1% 1-butene in air. The catalyst charge was 10 ml in volume. The catalyst particle size was 12–20 mesh. A Pyrex glass reactor was preferred to an 18/8 stainless-steel reactor because 18/8 stainless steel is reported to cause maleic anhydride decomposition (7). Details on the gas chromatographic analysis are reported elsewhere (8).

The oxidation of propylene was accomplished in an 18/8 stainless-steel fixed-bed reactor of 5.4-mm i.d. provided with an axial thermocouple. Also in this case the catalyst charge was 10 ml in volume. The catalyst particle size was 35 to 52 mesh. The feed consisted of 6.5% C_3H_6 and 13% oxygen (the balance being nitrogen) at a 400-ml min^{-1} total gas flow. The reactants and the products were analyzed by gas chromatography on different columns: a molecular sieve column of 1.2-m length at room temperature for O_2, N_2, and CO and a Poropak Q silanized 2-m-long column at 150°C for air, CO_2, H_2O, propylene, acrolein, and other oxidized products.

Details for infrared (ir), Raman (R), and X-ray measurements are given elsewhere (8). The surface area was determined with the area meter "Strölein" instrument by the BET method using nitrogen at −195°C as the adsorbate.

In this paper conversion means percentage of hydrocarbon which is converted to oxidized products, selectivity to a given product means percentage of hydrocarbon
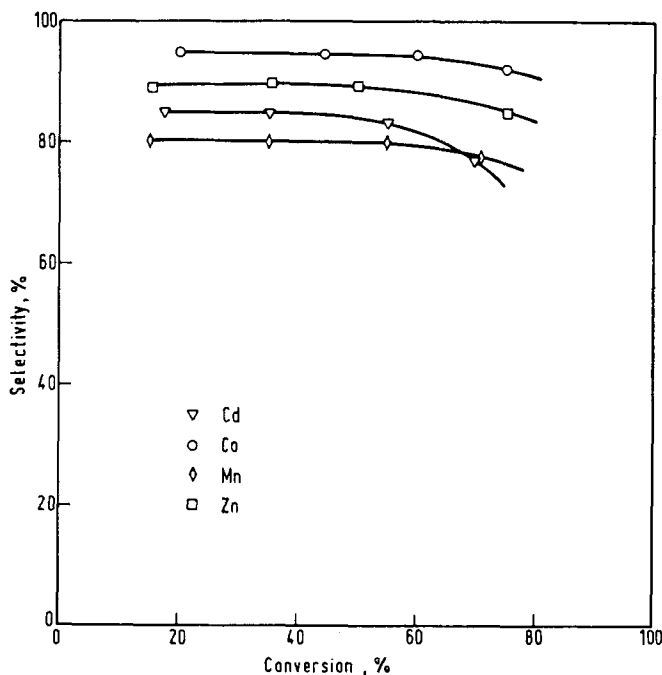

FIG. 1. Effect of 1-butene conversion on butadiene selectivity at GHSV = 600 in the 350 to 420°C range for CdTeMoO$_6$(▽), CoTeMoO$_6$(○), MnTeMoO$_6$(◇), and ZnTeMoO$_6$(□).
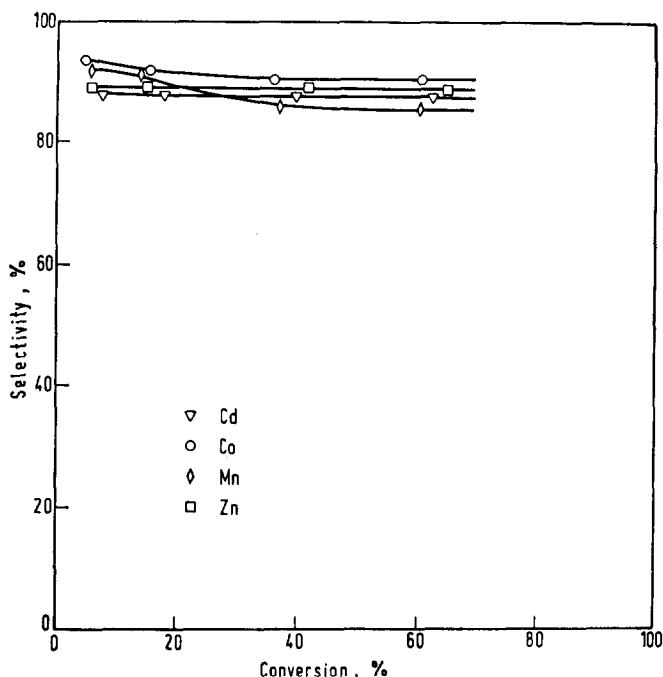
FIG. 2. Effect of propylene conversion on acrolein selectivity at GHSV = 2400 in the 350 to 470°C range for CdTeMoO$_6$(∇), CoTeMoO$_6$($\bigcirc$), MnTeMoO$_6$($\Diamond$), and ZnTeMoO$_6$($\square$).

converted to that product, and gas hourly space velocity (GHSV) means total gas volume fed per catalyst volume per hour.

RESULTS

Conversion–selectivity plots for the oxidation of 1-butene and propylene over the investigated catalysts are displayed in Figs. 1 and 2, respectively. Conversion variations were achieved by varying the inlet temperature between 350 and 470°C at constant GHSV.

For all the ternary oxide compounds, both the reactions are quite selective even at high conversions (60–80%). The lines drawn in Fig. 1 show selectivities of about 80 to 95%, and those in Fig. 2 of about 85 to 90%. The by-products in the oxidation of butenes are carbon oxides and frequently maleic anhydride, with small amounts of crotonaldehyde, furan, and other unidentified compounds. Appreciable amounts of maleic anhydride were found over MnTeMoO$_6$ (about 10% selectivity) and to a lower extent over ZnTeMoO$_6$ and CoTeMoO$_6$ (about 2% selectivity). The by-products in the oxidation of propylene are mainly carbon oxides; small amounts of acetaldehyde are also formed.

X-ray, ir, and R spectroscopies were employed in order to investigate the structures of the four ternary oxide catalysts for relation to their catalytic efficiency. The X-ray powder diffraction patterns are given in Table 1. They have been indexed on the basis of a tetragonal unit cell for CdTeMoO$_6$ (9) and orthorombic unit cell for CoTeMoO$_6$, MnTeMoO$_6$, and ZnTeMoO$_6$ (10); cell parameters are given in Table 2. The ir and R spectra are also shown in Figs. 3 and 4, respectively. ATR spectroscopy was also employed as a surface-sensitive technique; the spectra did not evidence variations in the position and relative intensity of the bands.

DISCUSSION

Figures 1 and 2 clearly indicate that $CdTeMoO_6$, $CoTeMoO_6$, $MnTeMoO_6$, and $ZnTeMoO_6$ represent a new class of highly selective catalysts for the allylic oxidation of olefins. Their selectivity–conversion lines compare well with those reported for known effective catalysts such as bismuth molibdate (11). Indeed, in the case of the oxidation of propylene, the selectivity at the same conversion levels is slightly higher while the activity under comparable experimental conditions (e.g., GHSV = 2400, T = 470°C for $MeTeMoO_6$; GHSV = 2500, T = 460°C for bismuth molybdate) is lower (60–65 vs 85%) but still comparable.

Maleic anhydride formed over $MnTeMoO_6$ could arise from the presence of traces of $MnMoO_4$ (6) in the catalyst, due

TABLE 1

X-ray Powder Diffraction Patterns (d Values, Angstroms) of $CdTeMoO_6$, $CoTeMoO_6$, $MnTeMoO_6$, and $ZnTeMoO_6$

$CdTeMoO_6$		$CoTeMoO_6$		$MnTeMoO_6$		$ZnTeMoO_6$	
9.034	(25)	8.85	(10)	8.98	(9)	8.91	(8)
4.522	(12)	4.42	(33)	4.47	(50)	4.46	(27)
3.729	(16)	3.64	(52)	3.69	(52)	3.64	(40)
3.448	(48)	3.38	(33)	3.41	(30)	3.40	(9)
3.015	(18)	3.33	(19)	3.38	(19)	3.37	(27)
2.88	(100)	2.955	(5)	2.985	(9)	3.33	(19)
2.641	(23)	2.817	(100)	2.846	(100)	2.97	(5)
2.62	(11)	2.630	(17)	2.647	(14)	2.82	(100)
2.348	(4)	2.572	(7)	2.600	(9)	2.628	(14)
2.284	(5)	2.550	(7)	2.580	(7)	2.585	(5)
2.263	(9)	2.533	(14)	2.570	(12)	2.518	(13)
1.988	(22)	2.295	(7)	2.322	(7)	2.300	(5)
1.870	(28)	2.257	(14)	2.276	(14)	2.263	(6)
1.866		2.211	(7)	2.241	(11)	2.227	(5)
1.720	(11)	2.199	(10)	2.230	(8)	2.194	(5)
1.714	(11)	2.065	(7)	2.084	(4)	2.064	(4)
1.643	(10)	2.040	(8)	2.062	(5)	2.050	(4)
1.630	(11)	2.029	(5)	2.055	(4)	1.968	(5)
1.588	(5)	1.962	(7)	1.981	(7)	1.921	(5)
1.567	(19)	1.920	(9)	1.947	(8)	1.820	(18)
		1.893	(6)	1.914	(4)	1.806	(6)
		1.822	(18	1.844	(21)	1.685	(6)
		1.806	(7)	1.828	(6)	1.680	(7)
		1.688	(11)	1.710	(7)	1.668	(5)
		1.665	(11)	1.705	(9)	1.601	(5)
		1.607	(7)	1.692	(9)	1.591	(5)
		1.590	(9)	1.688	(9)	1.553	(12)
		1.552	(17)	1.670	(4)	1.507	(10)
		1.509	(16)	1.612	(8)		
				1.609	(5)		
				1.564	(13)		
				1.531	(11)		

TABLE 2

Cell Parameters for $CdTeMoO_6$, $CoTeMoO_6$, $MnTeMoO_6$, and $ZnTeMoO_6$[a]

$CdTeMoO_6$	$CoTeMoO_6$	$MnTeMoO_6$	$ZnTeMoO_6$
a = 5.279	a = 5.262	a = 5.294	a = 5.255
	b = 5.062	b = 5.139	b = 5.044
c = 9.056	c = 8.857	c = 8.960	c = 8.909

[a] From refs. (9) and (10). Values are given in angstroms.

to incomplete solid-state reaction. Thus the four metal tellurium molybdates are specific catalysts for butadiene and acrolein. Actually, it is certainly worth noting that butadiene and acrolein do not undergo complete oxidation at high temperatures. The similar catalytic behavior of these systems is probably related to some common properties.

$CoTeMoO_6$, $MnTeMoO_6$, and $ZnTeMoO_6$ are isotypic compounds [orthorombic unit cell, symmetry space group $P2_12_12$ (10)] while, strictly speaking, $CdTeMoO_6$ is not [tetragonal unit cell, possible space groups $P4/n$ or $P4/nm$ (9)]. However, the strong analogies in the X-ray diffraction patterns (d values and relative intensities) result in similar unit cell dimensions as shown in Table 2, and indicate that the positions of Me, Te, Mo, and O atoms in the structures are also similar, although a geometrical arrangement with higher symmetry is achieved in $CdTeMoO_6$.

Further analogies in the structural features of the four metal tellurium molybdates are shown by ir and R spectra. The spectra display very close general patterns which indicate strong analogies in the Te–O and Mo–O bond geometries.

We can thus conclude that the structural properties could be the looked for properties primarily responsible for the catalytic behavior of the investigated systems.

It is interesting to note that Cd-, Mn-, and Co-molybdates are poorly selective in the oxidation of olefins and they also differ in activity (5), while the metal tellurium molybdates are highly specific for allylic oxidation products and show similar ac-
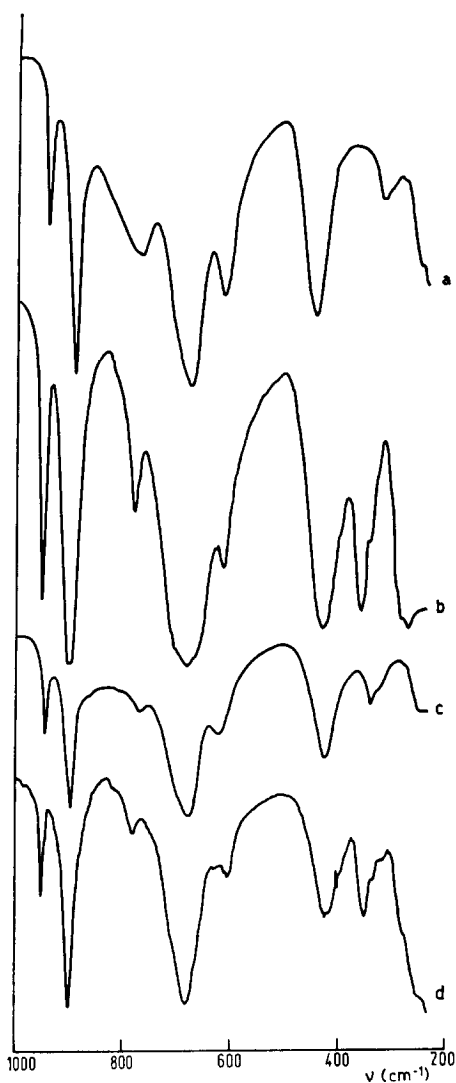
FIG. 3. Infrared spectra of CdTeMoO₆(a), CoTeMoO₆(b), MnTeMoO₆(c), and ZnTeMoO₆(d).

tivity. The problem arises then as to which might be the difference in the nature of active centers of the two classes of catalysts.

The Mo=O bonds were proposed to be responsible for the allylic oxidation in the case of pure molybdates (12, 13). The ir and R bands at 950 and 890 cm⁻¹ in the spectra of all the investigated metal tellurium molybdates together with the band at 380 cm⁻¹ (present as a shoulder of the broad 440-cm⁻¹ absorption band in
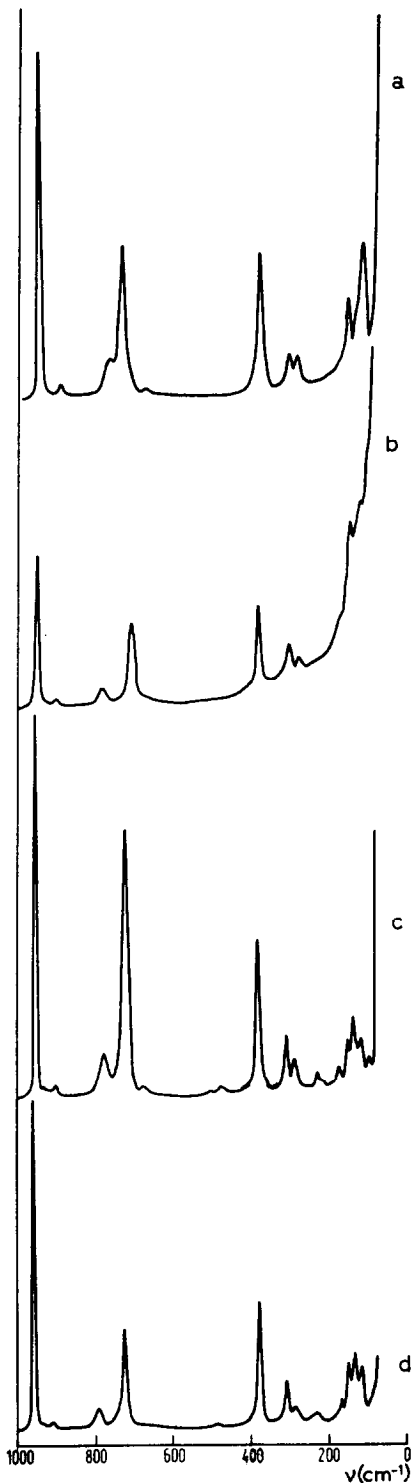
FIG. 4. Raman spectra of CdTeMoO₆(a), CoTeMoO₆(b), MnTeMoO₆(c), and ZnTeMoO₆(d).

the ir) indicate the presence of *cis*-MoO_2 groups with high Mo–O double-bond character (*1, 2*). The ATR spectra confirmed that MoO_2 groups are also likely present at the surface. Such groups with the same double-bond character are not present in pure molybdates. Co–, Mn–, and Zn–MoO_4 do show ir and R bands in the 900- to 1000-cm^{-1} range but at different frequencies while $CdMoO_4$ does not show any band in this region.

Cis-MoO_2 groups with high Mo–O double-bond character might provide two contiguous points for the removal of hydrogen atoms. Therefore, they could account for the high selectivity in allylic oxidation reactions, according to a mechanism involving first and second hydrogen removal followed, in the case of propylene, by oxygen insertion (*14*).

However, it is interesting to recall that TeO_3 by itself is active and selective in the oxidation of butene up to 300 to 350°C (*8*) where it transforms into inactive TeO_2 (*8, 15*).

Therefore, active and selective sites could also be directly related to tellurium. Possibly they could be Te(VI) sites somehow stabilized over 300 to 350°C. Although tellurium is present as Te(IV) in the title compounds, Te(VI) could still occur in small quantities in the structure of the metal tellurium molybdates as partially substituted to Mo(VI). Indeed the radii of the two cations are close. It is unlikely that Te is present in oxidation states lower than IV considering that Te(IV) and Te(VI) are the more stable ones and that we never found the formation of metallic tellurium. Furthermore, Sloczynski recently reported that $CoTeMoO_6$ is a stable product of the reduction of $Co_4TeMo_3O_{16}$ (*16*). This fact suggests that the ternary oxide compounds are stable under reducing conditions.

As a last remark we note that Cd, Co, Mn, and Zn ions, by occupying certain positions in the lattice, allow the existence of the four metal tellurium molybdates as well-defined compounds. Nevertheless, there is no evidence that these ions play a direct specific role in the mechanism of butene and propylene oxidation. Indeed the catalytic behavior of the ternary oxide compounds does not change with the metal ion, while the corresponding pure molybdates display some marked differences both in activity and selectivity.

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