# Mössbauer and E.S.R. Investigations of Tellurium Containing Oxides

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*Compounds from the tellurium–molybdenum–oxygen and tellurium–vanadium–oxygen systems have been investigated by E.S.R. and $^{125}Te$ Mössbauer spectroscopy. The data are interpreted in terms of the cationic oxidation states and their environments in the mixed oxide structures. The results are associated with the catalytic properties of these materials for the selective oxidation and ammoxidation of hydrocarbons.*

## Introduction

The phase compositions and properties of materials in the tellurium–molybdenum–oxygen [1–11] and tellurium–vanadium–oxygen [12–19] systems have recently been the subject of several careful investigations with the structural properties of $\alpha$-$Te_2MoO_7$ [5, 7], $TeMo_4O_{13}$ or $TeMo_5O_{16}$ [6], $\alpha$-$TeVO_4$ [17], $\beta$-$TeVO_4$ [18] and $V_2Te_2O_9$ [19] having received special attention. The two tellurium-molybdenum oxides have also been examined by XPS, infrared, Raman and diffuse reflectance spectroscopy [8] and, whilst this study was in progress, by E.S.R. [10, 11].

It is interesting that the catalytic properties of materials in the tellurium–molybdenum–oxygen system for the selective oxidation and ammoxidation of olefins [20–26] appear to be superior to those of other mixed oxides containing tellurium [27]. It is also pertinent to record that $Te_2MoO_7$ has been identified as the active phase in tellurium–molybdenum oxides [26], and to note attempts to associate morphological, structural and textural properties of tellurium–molybdenum oxides with their catalytic character [4, 26] and the significance which has been attributed [22] to factors which may influence cationic reduction and oxidation in these materials.

Mössbauer spectroscopy is a powerful technique by which tellurium oxidation states and cationic environments can be examined whilst paramagnetic molybdenum and vanadium species are readily detected by E.S.R. We have therefore examined some mixed oxides containing tellurium and either molybdenum or vanadium by Mössbauer spectroscopy and E.S.R. to elucidate further solid state properties which may influence catalytic character.

## Experimental

Samples of $\alpha$-$Te_2MoO_7$, $TeMo_5O_{16}$ and $V_2Te_2O_9$ were prepared by methods previously described [2, 3, 15] and initially supplied by Professor Dr. J. C. J. Bart.

X-ray diffraction data were recorded with a Philips vertical goniometer (PW 1050/70) using $CuK_\alpha$ radiation. E.S.R. spectra were recorded at 298 K with a Hilger and Watts instrument operating at 9.4 GHz and $g$-values measured relative to DPPH (diphenylpicrylhydrazyl, $g$ = 2.0036). Tellurium-125 Mössbauer spectra were recorded at 4.2 K using a $^{125}Sb/Cu$ source and a conventional constant acceleration spectrometer.

## Results and Discussion

The $^{125}Te$ Mössbauer parameters recorded in Table I are all very similar with chemical isomer shifts characteristic of tellurium(IV) in oxide environments [28, 29].

The detection in the spectra from $Te_2MoO_7$ and $TeMo_5O_{16}$ of single quadrupole split tellurium(IV) resonances confirms recent assignments based on other spectroscopic and structural data [8]. The E.S.R. spectrum from $Te_2MoO_7$ showed a single signal with a $g$-value of 2.0036 corresponding to that of DPPH (diphenylpicrylhydrazyl). The signal disappeared when the material was heated to 500 °C for 12 hours. Similar E.S.R. results have been recorded

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TABLE I. Tellurium-125 Mössbauer Parameters.

| Compound | $\delta^a \pm 0.12$ /mm $s^{-1}$ | $\Delta \pm 0.2$ /mm $s^{-1}$ | $\Gamma$ /mm $s^{-1}$ |
|---|---|---|---|
| $Te_2MoO_7$ | 0.64 | 6.6 | 7.8 |
| $TeMo_5O_{16}$ | 0.45 | 6.4 | 7.3 |
| $Te_2V_2O_9$ | 0.66 | 6.7 | 6.9 |

[a]$\delta$ relative to $^{125}I/Cu$.

from $Te_2MoO_7$ formed either by oxidation of molybdenum ditelluride at 600 °C and 630–650 °C [11] or by partial hydrogen reduction of $Te_2MoO_7$ at 320 °C [10]. Although we do not dispute the validity of the interpretation [10, 11] of these spectra in terms of molybdenum(V) we note the similarity between our results and observations recorded during E.S.R. investigations of catalytically active tin–antimony oxides [30] and various metal oxides [31–34] which have been interpreted in terms of trapped electrons and anionic vacancies. There can be little doubt that all three sets of E.S.R. results are consistent with data recorded from XPS [8] which were interpreted in terms of molybdenum(VI) in $\alpha$-$Te_2MoO_7$ and the description of the compound as $Te_2$-(IV)Mo(VI)$O_7$. However, the possibility that the E.S.R. signal recorded from $Te_2MoO_7$ emanates from electrons trapped at oxygen vacancies which are removed by annealing in air is quite consistent with the reported [2] increase in *n*-type semiconductivity and oxygen loss from molybdenum(VI) oxide on addition of tellurium(IV) oxide and observations [35] of superficial oxygen ion vacancies in molybdenum(VI) oxide. In this respect it is relevant to note that surface acidity and basicity has been associated with the catalytic properties of solid oxides [36] and trapped electrons have been envisaged as surface basic sites [37] in oxidation and ammoxidation catalysts. Hence the presence of trapped electrons in $Te_2MoO_7$, which has been identified [26] as the active phase in tellurium–molybdenum oxide ammoxidation catalysts, may be a significant feature of its catalytic character.

The Mössbauer spectral linewidths are slightly broader than expected for tellurium(IV) in well crystallised materials containing tellurium in one type of chemical environment. The observation is particularly true for the material of composition $Te_2MoO_7$ which has been shown by X-ray structure determination to contain tellurium in two different sites [5, 7]. However, the differences in the coordination around tellurium in these tellurium-molybdenum oxides [5–7] appears to be insufficient to cause distinguishable differences in the individual quadrupole splittings.

Given that several recent structural models of tellurium(IV) oxides [38–40] have assumed the stereochemical activity of the lone pair of electrons, it is appropriate to give more attention to the chemical isomer shift data which, being sensitive to the *s*-electron density at the nucleus, might reasonably be expected to reflect the electron distribution in these mixed oxides. It is clear that the chemical isomer shifts are smaller than those reported for the octahedral $TeX_6^{2-}$ (X = Cl, Br, I) species which have been interpreted [41] in terms of a $5s^2$ lone pair and 3-centre 4-electron tellurium–halogen bonding involving tellurium *5p* orbitals. Since $\Delta R/R$ for the $^{125}Te$ transition is positive [42] the chemical isomer shift data are consistent with the participation of tellurium *5s* electrons in the bonding as occurs in other compounds containing tellurium(IV) in oxygen environments [28, 29]. Indeed, calculations based on tellurium(IV) oxide have indicated *ca.* 10% s-character in the bonding orbitals [29]. However, the chemical isomer shifts of the coloured tellurium–molybdenum oxides and tellurium–vanadium oxide reported here are, like those of other coloured mixed oxides containing tellurium [28, 29], smaller than those reported for white pure tellurium(IV) oxide [29, 41, 43–46]. Although great caution must be exercised in attributing significance to small differences in chemical isomer shifts the lower values of $\delta$, which correspond to lower *s*-electron densities at the tellurium nuclei, and the introduction of colour into the mixed oxides may be interpreted in terms of the delocalisation of electrons into low energy conduction bands. Indeed, low $^{125}Te$ Mössbauer chemical isomer shifts have also been observed in coloured organotellurium(IV) halides [47], and substituted tellurium(II) acetylacetonates [48] and attributed to the population by non-bonding *s*-electrons of conduction bands. Furthermore, the chemical isomer shift data recorded from coloured compounds containing other *p*-block elements such as tin and antimony have revealed similar effects and have been interpreted [49–54] in terms of the direct population of low energy conduction bands by non-bonding valence electrons.

In view of the foregoing it would seem significant that the chemical isomer shift recorded from dark violet $TeMo_5O_{16}$, which has been considered in terms [8] of distinct molybdenum-(V) and -(VI) sites, is more negative than that of yellow $\alpha$-$Te_2MoO_7$. The E.S.R. spectrum recorded from $TeMo_5O_{16}$ was characterised by a broad resonance similar to that recorded earlier [10, 11] and interpreted in terms of exchange interactions between molybdenum(V) ions in materials described [8, 10] as involving electron delocalisation over some oxomolybdenum sites. We suggest that the low Mössbauer chemical isomer shift and the E.S.R. spectrum from $TeMo_5O_{16}$ are indicative of the delocalisation of predominantly

*5s* non-bonding electrons from tellurium(IV) over molybdenum cation sites which may, or may not, result in formal reduction of molybdenum(VI). Similar effects have been observed during $^{119}Sn$ and $^{121}Sb$ Mössbauer studies of catalytically active tin-antimony oxides [55, 56].

It is also pertinent to consider the compound $Te_2V_2O_9$ which has been described [19] in terms of tellurium(IV) and vanadium(V). Although our Mössbauer results confirm the presence of tellurium-(IV), indeed the parameters are in good agreement with those reported [28] for $Te_2V_2O_9$ at 80 K, the E.S.R. spectrum showed hyperfine interactions similar to that observed in the spectra of other materials containing vanadium(IV) [57, 58]. Since our X-ray diffraction pattern from the material was consistent with that reported [15] for $Te_2V_2O_9$ and gave no evidence of a vanadium-containing impurity phase we presume that some vanadium in $V_2Te_2O_9$ adopts a lower than expected oxidation state. Given the influence which has been attributed to tellurium on the nature of molybdenum in molybdenum oxides [22, 26], it is reasonable to suggest that subtle electronic interactions between tellurium(IV) and molybdenum(VI) in mixed oxide ammoxidation catalysts may contribute to their superior catalytic properties as compared with other mixed oxides containing tellurium.

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