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# THERMAL DECOMPOSITION AND THE CREATION OF REACTIVE SOLID SURFACES.
# V. THE GENESIS COURSE OF THE $WO_3$ CATALYST FROM ITS AMMONIUM PARATUNGSTATE PRECURSOR

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## ABSTRACT

The thermal decomposition of ammonium paratungstate $(NH_4)_{10}(H_2W_{12}O_{42})\cdot 7H_2O$ to the onset of formation of $WO_3$ was studied using thermogravimetric and differential thermal analyses. Intermediate solid products were obtained by calcination at 155–500 °C and subsequently analyzed using infrared spectroscopy and X-ray diffractometry. The gaseous products were identified by infrared spectroscopy. The results obtained together with molecular stoichiometry calculations, based on weight losses determined thermogravimetrically, could help in proposing a scheme for the course of decomposition.

## INTRODUCTION

Heterogeneous catalysts are often produced by thermal decomposition of supported or unsupported inactive solid precursors. Dealing with various precursor/catalyst systems, parts I–IV of the present comprehensive investigation [1–4] concluded that the existence of special fast transport paths (e.g. surfaces, pores, grain boundaries, etc.) for the precursor volatile constituents eventually leads to materials possessing pores, lattice imperfections and other characteristics that are necessary for surface reactivity.

This work presents and discusses the results of a characterization study of the thermal decomposition course of ammonium paratungstate (APT) to the onset of formation of the $WO_3$ catalyst. The application of APT as a precursor (see for example ref. 5), and the $WO_3$ thus produced as a catalyst (particularly for metathesis reactions) (see for example ref. 6) is well documented in the literature. The characterization studies that have been published [7–9] were concerned with the catalyst produced rather than the genesis course.

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A detailed structural analysis of the APT precursor $(NH_4)_{10}(H_2W_{12}O_{42}) \cdot 7H_2O$ has been reported [10]. It revealed that APT crystallizes in space group *pbca* with a pseudo symmetry $2/m$. The paratungstate ion $(H_2W_{12}O_{42})^{10-}$ (not $(H_{10}W_{12}O_{45})^{10-}$ as earlier presumed [11]) consists of four corner-sharing groups, each containing three edge-sharing $WO_6$ octahedra. $^1H$-nuclear magnetic resonance broad-line spectra [12] have indicated that the non-acid protons occupy the interior of the isopoly anion. Each paratungstate ion is connected via $NH_4^+$ ions to ten others. Bond lengths, angles, unit cell parameters and other relevant structural data have also been reported [10].

In the present investigation, the thermal decomposition behavior of APT on heating to 600 °C was studied by thermogravimetric (TG) and differential thermal (DTA) analyses. The gaseous decomposition products were identified by means of infrared (IR) spectroscopy, whereas the solid materials yielded at intermediate temperatures were subjected to IR and X-ray diffraction (XRD) analyses.

## EXPERIMENTAL

### *Materials*

The APT precursor $(NH_4)_{10}(H_2W_{12}O_{42}) \cdot 7H_2O$ was an AR-grade ($\geqslant$ 99% pure) Fluka (Switzerland) product. Its calcination products were obtained at 155, 210, 270, 320, 370, 500 and 600 °C for 3 h, in a still atmosphere of air. The calcination temperatures were chosen on the basis of the thermal analysis results (see below). For reference purposes, a sample of $WO_3$ supplied by Degussa (W. Germany) was employed. Prior to analysis, all materials used were kept dry over $P_2O_5$.

### *Apparatus and techniques*

The TG and DTA analyses of the decomposition of APT on heating at 5 °C $min^{-1}$ to 600 °C, in a dynamic (20 ml $min^{-1}$) atmosphere of air, and IR spectroscopy of KBr-supported solid products of the decomposition, yielded at 155–600 °C for 3 h, were performed using the apparatus and techniques described previously [13].

The XRD analysis of APT and its decomposition products were carried out by means of a Model JSX-60PA JEOL diffractometer (Japan), equipped with a source of Ni-filtered Cu $K_\alpha$ radiation. For identification purposes, diffraction patterns obtained were matched with ASTM standards.

IR-identification of the gaseous decomposition products was done with the help of spectra taken from the gas phase surrounding a self-supporting wafer of APT, being heated at 10 °C $min^{-1}$ to various temperatures

(100–400 ° C, for 10 min) in a specially designed IR cell [14] equipped with KBr windows.

## RESULTS AND DISCUSSION

### *Thermal events encountered throughout the APT decomposition course*

The TG and DTA curves for APT are shown in Fig. 1. The TG curve indicates that the material suffers ca. 11.5% loss of its original weight in four overlapping steps with maxima at 120 (1.5%), 195 (2%), 265 (6.5%) and 359 ° C (1.5%). The DTA curve reveals an endothermic nature for the first two steps (max. at 120 and 195 ° C), an exothermic composite character for the third (at 265 ° C), and a slightly endothermic nature for the fourth step (at 359 ° C). Moreover, it discloses the occurrence at 386 ° C of a strongly exothermic process, i.e. immediately after the completion of the fourth weight loss step. Beyond this temperature range and up to 600 ° C no other thermal events were detectable. These results indicate that the decomposition of APT begins at 120 ° C and is completed at ca. 370 ° C, leaving a solid product that suffers nothing (up to 600 ° C) but a physical change near 386 ° C (i.e. in the immediate vicinity of its formation).

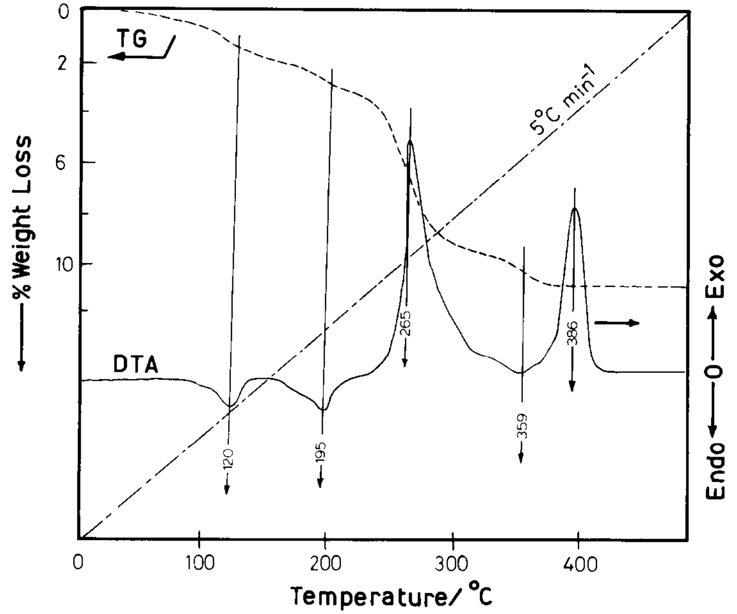

Fig. 1. TG and DTA curves of ammonium paratungstate decomposition on heating at 5 ° C $\min^{-1}$ in a dynamic atmosphere of air (20 ml $\min^{-1}$).

## *Analysis of the decomposition products*

### *The gas phase*

IR gas-phase spectra taken over the frequency range 4000–200 cm$^{-1}$ and at a resolution of 2.3 cm$^{-1}$, while heating APT at 10 °C min$^{-1}$ to 400 °C, are shown in Fig. 2. At 100 °C, the corresponding spectrum indicates the emergence of weak absorptions at 2355, and at 970 and 935 cm$^{-1}$ (doublet), the intensity of which was enhanced on increasing the decomposition temperature to 400 °C. The band at 2355 cm$^{-1}$ is diagnostic of the antisymmetric stretching vibration of $CO_2$ [15]; the characteristic band at 660 cm$^{-1}$ of the relevant bending mode is far more sensitive to the gas pressure [16]. Indeed, it can only be seen in the spectra obtained at $\geqslant$ 270 °C (Fig. 2). The doublet bands occur at frequencies (970 and 935 cm$^{-1}$) very close to those (968 and 932 cm$^{-1}$ [17]) characteristic for the symmetric bending vibrations of $NH_3$ molecules. Bands due to the symmetric stretching and the doubly degenerate bending modes of $NH_3$ vibrations show, respectively, at 3340 and

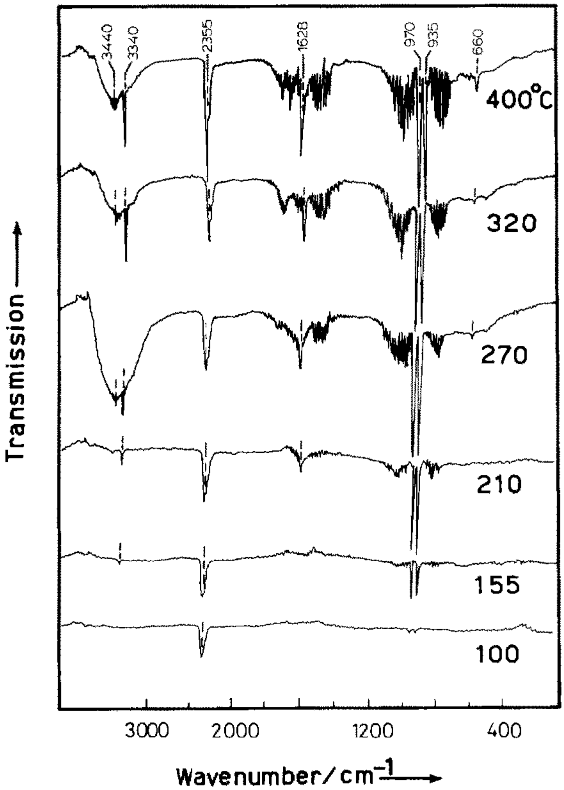

Fig. 2. IR spectra taken at a resolution of 2.3 cm$^{-1}$ from the gas phase surrounding ammonium paratungstate being heated at 10 °C min$^{-1}$ at the temperatures indicated for 10 min.

1628 cm$^{-1}$ in the 210 °C spectrum, in excellent agreement with literature data [17].

These results indicate that in the temperature range encompassing the first weight loss step (max. at 120 °C, Fig. 1), $CO_2$ dominated the gas phase, most probably at the expense of surface carbonaceous contaminants. However, at around the temperature range of the succeeding weight loss step (at 195 °C), $NH_3$ dominated.

As the decomposition temperature was increased to 270 °C, a temperature at which the third weight loss step (Fig. 1) is maximized, the spectrum obtained (Fig. 2) displays a strong and broad absorption band centered around 3440 cm$^{-1}$, in addition to the spectral features of $CO_2$ and $NH_3$. This absorption is considered [18] to be $\nu$OH stretching vibrations of hydrogen-bonded $H_2O$ molecules.

The associated $\delta$HOH bending vibrations have caused no absorption at 1650 cm$^{-1}$ [18]. This can be due either to a restriction of the free bending of the $H_2O$ molecules, imposed by an engagement in a stronger-than-normal type of hydrogen bonding with co-existing $NH_3$ molecules, or to the possibility that the vibrations of both the $H_2O$ bending and the doubly degenerate bending of $NH_3$ may contribute to the absorption at 1628 cm$^{-1}$. However, since the $NH_3$ symmetric bending vibration is far more intense than the degenerate one (cf. the 155 and 210 °C spectra), it does not seem likely that very much of the observed increase of absorption in this region (spectra obtained at $\geqslant 270$ °C) is caused by $NH_3$.

The gas phase spectra obtained after APT had been treated at $\geqslant 320$ °C maintained the band structure shown in the 270 °C spectrum with a decrease in the absorption around 3440 cm$^{-1}$. They additionally indicated the emergence of a weak, but significant, absorption (at 1650 cm$^{-1}$) in the $\delta$HOH region, thus revealing the existence of free $H_2O$ molecules.

Thus, gas phase spectra characterize the existence of two types of water molecules depending on the decomposition temperature: at 270 °C, $H_2O$ bonded to $NH_3$ molecules; and at $\geqslant 320$ °C, free $H_2O$ molecules coexist. In fact, the formation of ammonia hydrates, $NH_3 \cdot H_2O$ or $2NH_3 \cdot H_2O \simeq (NH_4)_2O$, has previously been identified by IR [19] and mass [20] spectra. The absence of an IR absorption band at 1400 cm$^{-1}$ (as is the case here, cf. Fig. 2), has led us to conclude that ammonia hydrates contain no $NH_4^+$ ions [19]. Waldron and Hornig [19] have therefore proposed that the ammonia hydrates are either bi- or trimolecular species including strong $NH \cdots O$ bonds, and that hydrogen atoms from $H_2O$ are also hydrogen bonded.

### *The solid state*

Results of the IR and XRD analyses of the solid decomposition products of APT, at various temperatures (155–500 °C) for 3 h are shown in Figs. 3 and 4.

The IR spectrum of the untreated APT (Fig. 3) displays bands assignable

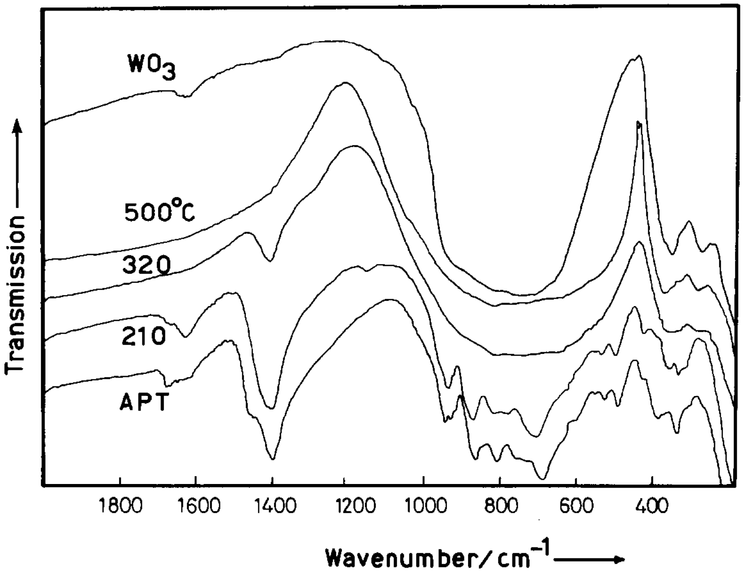

Fig. 3. IR spectra for ammonium paratungstate (APT) and its calcination products at the temperatures indicated for 3 h; the spectrum of reference (Degussa) $WO_3$ is inset for comparison purposes.

to polytungstates (at 930, 870, 690, and 600–300 cm$^{-1}$ [21]), $NH_4^+$ ions (at 1400 cm$^{-1}$ [22]), hydration water (at 1650 and $\leq 800$ cm$^{-1}$ [18]), and surface species of $CO_3^{2-}$ (at 1455 cm$^{-1}$ [23]) and $HCO_3^-$ (at 1680, 950, 810, and 750 cm$^{-1}$ [23]) contaminants. In the high frequency region (not shown in Fig. 3), the spectrum exhibited a composite, broad absorption of three components at 3365, 3220 and 2955 cm$^{-1}$. These absorptions had respectively been assigned [19] to N–H, O–H and NH $\cdots$ O vibrations, associated with $(NH_4)_2O$-like species. These results suggest that the ammonia content of APT is contained in $NH_4^+$ ions and $(NH_4)_2O$ species. The structural analysis made by Allmann [10] has supportively disclosed that a part of the $NH_4^+$ ions exchanges strong interactions with some of the hydration water. The length of the bonds established (2.69 Å) is very similar to that (2.8 Å) spectroscopically determined [19] for NH $\cdots$ O bonds in $(NH_4)_2O$ species.

The spectrum taken from the decomposition product at 210 °C (Fig. 3) showed an almost complete elimination of the characteristic spectral features due to $CO_3^{2-}$ and $HCO_3^-$ surface contaminants (in agreement with the appearance of $CO_2$ in the gas phase (Fig. 2)), and a weakening of those due to $(NH_4)_2O$ and $NH_4^+$ ions (in consequence of the existence in the gas phase of $NH_3$), whereas the band structure of the polytungstate and hydration water remained unchanged. The corresponding XR diffractogram (Fig. 4), on the other hand, displays a pattern similar to that of APT (ASTM No. 25-45) with a general slight shift towards shorter *d*-spacings. This result

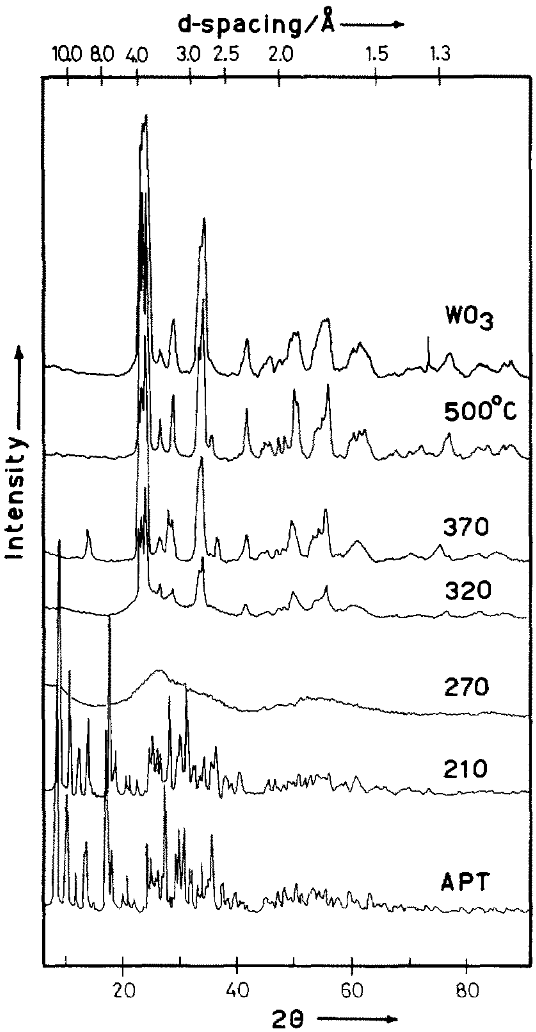

Fig. 4. XR powder diffractograms (Cu $K_\alpha$ radiation) for ammonium paratungstate (APT) and its calcination products at the temperatures indicated for 3 h; the diffractogram of reference (Degussa) $WO_3$ is shown for comparison purposes.

indicates that the release of $NH_3$ (Fig. 2) via the second weight loss step (at 195 °C, Fig. 1) has led to a sort of lattice contraction.

The XRD analysis (Fig. 4) of the decomposition product yielded at 270 °C, i.e. via the third weight loss step (Fig. 1), indicated an almost complete destruction of the APT lattice, giving rise to an amorphous product. Supportive results were found in a corresponding IR analysis (not shown in Fig. 3). Additionally, the IR analysis indicated almost complete disappearance of the bands due to $(NH_4)_2O$, and a considerable decrease in the absorption intensity of $NH_4^+$ ions at 1400 $cm^{-1}$.

The XR diffractogram of the material produced at 320 °C (Fig. 4), i.e. just prior to the commencement of the fourth, and last, weight loss step (at 359 °C), exhibited, however weakly, a pattern very similar to that shown for $WO_3$ (Fig. 4 and ASTM No. 32-1394). The notable broadness of the peaks indicates a highly dispersed state for this newly produced $WO_3$. The corresponding IR spectrum (Fig. 3) compatibly showed a blackout absorption at $< 1200\ cm^{-1}$, similar to that exhibited by the reference $WO_3$ (also shown in Fig. 3).

The formation and crystallization of $WO_3$ are shown (Figs. 3 and 4) to have advanced markedly as the decomposition temperature was elevated to $\geqslant 400\ °C$. In fact, $WO_3$ obtained at 500 °C gave rise to XRD characteristics (viz. well resolved, narrow peaks) indicative of a crystallization state far more advanced than that exhibited by the reference (Degussa) $WO_3$ (Fig. 4). These observations presume that the fourth weight loss step ( ~ 1.5%) has led to the formation of highly dispersed $WO_3$, and that the succeeding exotherm (at 386 °C, Fig. 1) marks its crystallization.

### *A scheme for the decomposition course*

The results described above, together with molecular stoichiometry calculations based on weight losses determined by the TG analysis, have helped to formulate the following scheme for the APT decomposition course.

#### *100–120 °C*

In this range surface $CO_3^{2-}$ and $HCO_3^-$ groups as well as a minute amounts of $(NH_4)_2O$ species are eliminated, thus releasing $CO_2$, $NH_3$ and $H_2O$ into the gas phase, and causing ca. 1.5% loss of the original weight.

#### *190–210 °C*

In this range the release of $NH_3$ and $H_2O$ into the gas phase is increased. The total weight loss determined ( ~ 3.5%) is slightly higher than that (3.2%) anticipated for the conversion of APT $(NH_4)_{10}(H_2W_{12}O_{42}) \cdot 7H_2O$ to an ammonium metatungstate $(NH_4)_5(H_2W_{12}O_{40}) \cdot 7H_2O$. Such a conversion may account for the lattice contraction'indicated by the XRD analysis (Fig. 4).

#### *240–290 °C*

In this range the decomposition brings the total weight loss up to ca. 10.0% and increases the proportion of $H_2O$ in the gas phase, most likely at the expense of the hydration water. The IR analysis of the solid material yielded indicated a retention of some $NH_4^+$ ions, whereas the XRD showed a collapse of the polytungstate lattice leading to an amorphous substance. A similar material obtained by roasting APT at 270–300 °C for 10 h was transformed to ammonium metatungstate by acidification (at $pH \simeq 3.6$) in aqueous $NH_4^+$ or $H^+$ solutions [24]. Accordingly, one may infer that on eliminating $NH_4^+$ ions in the temperature range shown the polytungstates must have undergone a further polymerization to give larger anions in a highly dispersed state. A similar situation has been reported [25] during the heating of $(NH_4)_2CrO_4$ to give $(NH_4)_2Cr_2O_7$, on the way to $CrO_3$.

### *≃ 370 °C*

At this temperature the decomposition course is rounded off by a further slight weight loss step (~ 1.5%) leading to the formation and subsequent crystallization (at 386 °C) of $WO_3$. The total weight loss determined (11.5%) is just slightly lower than that (12.6%) expected from a complete conversion of APT to $WO_3$. Particle size and crystallinity of $WO_3$, thus produced, advance notably with a further increase of the calcination temperature to 500 °C.

## REFERENCES

1 M.I. Zaki and M. Abdel-Khalik, Thermochim. Acta, 78 (1984) 29.
2 M.I. Zaki and M. Abdel-Khalik, Colloids Surfaces, 13 (1985) 323.
3 M.I. Zaki and R.B. Fahim, J. Thermal Anal., 31 (1986) 825.
4 M.I. Zaki and N.E. Fouad, Thermochim. Acta, 95 (1985) 73.
5 T.K. Kim, R.P. McClinitic and C.D. Vanderpool, U.S. Patent 4,612,180, 16 September 1986.
6 F.P.J.M. Kerkhof, J.A. Moulijn, R. Thomas and J.C. Oudejans, Stud. Surf. Sci. Catal., 2 (1979) 77.
7 F.P.J.M. Kerkhof, J.A. Moulijn and A. Heeres, J. Electron. Spectrosc. Relat. Phenom., 14 (1978) 453.
8 A.J. Van Roosmalen, D. Koster and J.C. Mol, J. Phys. Chem., 84 (1980) 3075.
9 B. Wazynska, M.B. Swierczynska and T. Jasiewicz, Mater. Elektron., 2 (1985) 7.
10 R. Allmann, Acta Crystallogr. Sec. B, B27 (1971) 1393.
11 I. Lindqvist, Acta Cryst., 5 (1952) 667.
12 V.I. Spicyn, H.J. Lunk, V.F. Čuvaev and I.D. Kolli, Z. Anorg. Chem., 370 (1969) 191.
13 M.I. Zaki and T. Baird, Reactivity Solids, 2 (1986) 107.
14 J.B. Peri and R.B. Hannan, J. Phys. Chem., 64 (1960) 1526.
15 C.N. Banwell, Fundamentals of Molecular Spectroscopy, McGraw-Hill, London, 2nd edn., 1972, p. 90.
16 R.H. Pierson, A.N. Fletcher and E.C. Gantz, Anal. Chem., 28 (1956) 1218.
17 K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley-Interscience, New York, 2nd edn., 1970, p. 91.
18 J.A. Gadsden, Infrared Spectra of Minerals and Related Inorganic Compounds, Butterworth, London, 1975, p. 15.
19 R.D. Waldron and D.F. Hornig, J. Am. Chem. Soc., 75 (1953) 6079.
20 I.H. Park, Bull. Chem. Soc. Jpn., 45 (1972) 2745.
21 J.A. Gadsden, Infrared Spectra of Minerals and Related Inorganic Compounds, Butterworth, London, 1975, p. 152.
22 T.C. Waddington, J. Chem. Soc., (1958) 4340.

23 J.A. Gadsden, Infrared Spectra of Minerals and Related Inorganic Compounds, Butterworth, London, 1975, p. 23.
24 J.A. Powers and J.N. Christini, U.S. Patent 4,557,923, 10 December 1985.
25 A.K. Galwey, L. Pöppl and S. Rajam, J. Chem. Soc. Faraday Trans. 1, 79 (1983) 2143.