

Special Review

PHYSICO-CHEMICAL PROPERTIES OF CATALYSTS: THERMAL ANALYSIS, INFRARED SPECTROSCOPY, X-RAY DIFFRACTION AND MAGNETIC SUSCEPTIBILITY OF THE VANADATES OF ZINC, MANGANESE AND SILVER

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Thermal characteristics of the vanadates of zinc, manganese and silver have been studied by DTA and TG techniques and the different transition products thus obtained have been characterised by IR, X-ray diffraction and magnetic susceptibility data. Chemical analyses indicate the following compositions of these vanadates: (1) $Zn_2V_2O_7 \cdot 5H_2O$, (2) $Zn_3(VO_4)_2 \cdot 3H_2O$, (3) $Mn(VO_3)_2 \cdot 2H_2O$ and (4) Ag_3VO_4 . The DTA curves indicate that zinc pyrovanadate undergoes endothermic changes at 110–195, 265, 365, 440, 660° and one exothermic change at 485°. This system is diamagnetic which becomes completely paramagnetic after 660°. Zinc orthovanadate exhibits a number of endothermic peaks at 300, 470, 700, 815 and 930° respectively. This system is feebly paramagnetic and retains this property up to 930°. Manganese metavanadate undergoes endothermic changes at 240, 280–590, 830 and 880° respectively. This vanadate is paramagnetic and paramagnetism increases appreciably at 590° and remains constant up to 830°. Silver orthovanadate exhibits three endothermic changes at 180, 455 and 640°, respectively.

Bhattacharyya et al. have made exhaustive studies on the structural properties of a large number of solid catalysts by using the thermal analysis techniques (DTA, TG and DTG) supplemented by X-ray diffraction technique. The results were published in various journals and the important findings have recently been summarized in two review articles [1, 2].

In the present paper, the thermal characteristics of the vanadates of zinc, manganese and silver are presented.

Broun et al. [3] found zinc vanadates as the best catalysts for the synthesis of acetone from C_2H_2 at 450° and Miyazawa et al. [4] reported that zinc vanadate was quite active for vinyl acetate manufacture. Kurichika [5] and Nozu [6] noticed zinc orthovanadate to be effective catalyst for the synthesis of pyridine bases from C_2H_2 condensation with ammonia at 250–350°.

Broun et al. [3] found manganese vanadate as one of the selective catalysts for acetone synthesis from C_2H_2 at 450° and Sherman [7] reported that the compound could be used as a catalyst for the oxidation of anthracene to anthraquinone.

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Atarashi and Fukumo [8] used manganese vanadate as a catalyst for the formation of polythene by the polymerization of ethylene at 80–200°.

Fester et al. [9] reported that silver orthovanadate was quite efficient catalyst for the oxidation of ethyl alcohol to AcH, AcOH and CO₂ etc. at 360° and Yatani et al. [10] found it to be fairly active for the vapour phase oxidation of anthracene to anthraquinone. Ingram [11] used silver orthovanadate as a catalyst for micro-combustion of organic compounds and Stiles [12] reported it to be efficient for removal of thiophene from benzene. Lewis et al. [13] observed this catalyst to be of importance for the oxidation of picolines to nicotinic acid.

Studies on the thermal characteristics of the above vanadates using DTA and TG techniques have not been reported so far. Characterization of the different phases of the four vanadates when thermally treated at different temperatures by IR and X-ray diffraction techniques have also not been studied properly except the reports made by Brisi [14] that the crystal structure of silver orthovanadate is orthorhombic and by Bhattacharyya et al. [1] that silver metavanadate does not undergo any substantial change up to 350° i.e. before melting of the substance.

The object of undertaking this problem was to study the thermal characteristics of these vanadates by DTA and TG techniques and to identify the phase changes if any, by IR, X-ray diffraction and magnetic susceptibility measurements when the vanadates are subjected to various thermal treatment. An attempt has also been made to correlate, wherever possible, the structural properties of these vanadates with their catalytic activity.

Experimental

Preparation of the catalysts

All the chemicals used for the preparation of the catalysts were of Anala R quality.

Zinc pyrovanadate: 100 ml of 20% zinc sulphate solution (20 g/100 ml water) saturated at room temperature was slowly added (5 ml at a time) by stirring to a hot saturated solution of 5% ammonium metavanadate (10 g/200 ml water) at 80–90° (pH 5.2–6.7) followed by digestion for 45 min [15].

Zinc orthovanadate: Cold saturated solution of zinc sulphate (86.2 g/liter) was added slowly by stirring to a hot saturated solution of sodium orthovanadate (87.2 g/liter) at 80–85° (pH. 2–9.9) followed by digestion for 30 min.

Manganese metavanadate: 150 ml of manganese sulphate solution (15.1 g/150 ml water) saturated at room temperature was slowly added by stirring to a hot saturated solution of ammonium metavanadate (23.4 g/1500 ml water) at 70–80° followed by digestion for 30 min.

Silver orthovanadate: A dilute solution of silver nitrate was slowly added to a hot saturated solution of sodium orthovanadate with stirring until a little excess of the former was present in the solution.

All the substances were allowed to settle, filtered in a Buchner funnel, washed repeatedly with hot water until they were free from adsorbed soluble impurities, then dried in an air-oven at 110° for at least 24 hs.

Chemical analysis

Vanadium: V^{5+} in solution was analyzed in all the cases by redox titration with Mohr's salt in sulphuric acid medium using diphenyl-aminephosphoric acid indicator.

Zinc: Zn^{2+} in solution was analyzed in both the cases either as $ZnNH_4PO_4$ by precipitation with ammoniacal diammonium hydrogen phosphate and calcination at 105° or as $Zn_2P_2O_7$ by calcination at 700–800°.

Manganese: Mn^{2+} in solution was determined as $Mn_2P_2O_7$ by precipitation with diammonium hydrogen phosphate and calcination at 800°.

Silver: Ag^+ in solution was analyzed by titration of the nitric acid solution of silver orthovanadate with a standard ammonium thiocyanate solution, using ferrous ammonium sulphate as indicator.

Miscellaneous: Water was estimated in all the cases using Coleman Carbon-Hydrogen Analyser by absorption of water on anhydrous magnesium perchlorate. Zinc pyrovanadate and manganese metavanadate were subjected to the usual test of nitrogen, using Nitrogen Analyzer for detection of ammonia whereas orthovanadates of zinc and silver, to the usual test with zinc-uranyl acetate for detection of sodium ions. However, no ammonia or sodium ions were detected.

Differential thermal analysis (DTA)

DTA of all the catalysts were carried out in air using a manually operated DTA apparatus. The details of the experimental set up, furnace, sample holder, method of measurements, etc., were described by Bhattacharyya earlier [16, 17].

Thermogravimetric analysis (TG)

TG of all the vanadates were carried out in Stanton Mass Flow Thermobalance, Model MFH-5 with programmed heating rate 6.5°/min in an air atmosphere. The weights of the different catalyst samples for DTA and TG studies are given as follows:

| Sample weight | DTA | TG |
|----------------------|--------|-----------|
| Zinc pyrovanadate | 500 mg | 149.85 mg |
| Zinc orthovanadate | 500 mg | 12.09 mg |
| Manganese vanadate | 500 mg | 150.15 mg |
| Silver orthovanadate | 500 mg | 27.55 mg |

Infrared studies (IR)

The infrared absorption spectra of these catalysts preheated to following different transition temperatures at least for two hours in each case, were taken using a Perkin-Elmer Spectrophotometer in nujol medium. The IR spectrum was scanned in the region $625-4000\text{ cm}^{-1}$. The samples were examined at the following temperatures:

Zinc pyrovanadate: $110^\circ, 340^\circ, 440^\circ, 550^\circ, 710^\circ$.

Zinc orthovanadate: $110^\circ, 340^\circ, 580^\circ, 770^\circ, 1000^\circ$.

Manganese metavanadate: $110^\circ, 280^\circ, 590^\circ, 830^\circ$.

Silver orthovanadate: $110^\circ, 260^\circ, 380^\circ, 510^\circ, 620^\circ$.

X-ray diffraction studies

The X-ray diffractograms of the above-noted samples were obtained using a Philips Diffractometer with nickel filtered CuK radiation. The setting of the instrument was 50 KV/16 ma; gain 8/0.85; beam slit 3° ; detector 0.2; EL = 0.96 V; E and Eu out; range 200 C. P. S. (Linear); time constant 2 sec; scanning speed 20/min; paper $12''/\text{h}$.

Magnetic susceptibility measurements

Magnetic susceptibility measurements of the afore written samples were carried out in Cahn Electrobalance (a Faraday magnetic balance) at room temperature (24°) using mercuric cobalt tetrathiocyanate $\text{Hg Co} [(\text{NCS})_4]$, as calibrant.

Results and discussion

The compositions and the results of thermal analysis of all the vanadates are shown in Table 1.

Zinc pyrovanadate

Thermal analysis: DTA and TG curves of this compound are shown in Fig. 1. The DTA curve records a flat endothermic peak within the temperature range $110-195^\circ$ followed by two sharp endothermic changes at 265° and 365° . Then there appears a very small endothermic dent at 440° followed by one sharp exothermic peak at 485° and one sharp endothermic peak at 660° . The TG curve registers a total weight-loss amounting to 35.38% within $110-740^\circ$. The weight-loss registered in the TG curve up to 340° was calculated and found to be 21.90% which corresponds to the removal of five molecules of water from one molecule of $\text{Zn}_2\text{V}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$. The TG curve does not give any clear indication about the formation of intermediate stages in the course of dehydration. However, the DTA

Table I
Results of chemical composition and thermal analysis

| Substance | Composition | Formula | Results of thermal analysis | | | | |
|------------------------|---|----------------------------|-----------------------------|-------------------|--------------------------|-------------------|--------------------------|
| | | | Endothermic peak temp. °C | Range of temp. °C | Exothermic peak temp. °C | Range of temp. °C | % weight loss |
| Zinc pyrovanadate | Zn -- 37.9% | $Zn_2V_2O_7 \cdot 5H_2O$ | — | 110—195 | 485 | 460—510 | 21.90, within 110—340 °C |
| | V -- 29.56% | | 265 | 195—335 | | | |
| | H ₂ O -- 21.42% | | 365 | 340—410 | | | |
| Zinc orthovanadate | Zn -- 40.37% V -- 20.97% H ₂ O -- 12.33% | $Zn_3(VO_4)_2 \cdot 3H_2O$ | 440 | — | — | — | 13.48, within 440—740 °C |
| | | | 660 | 610—675 | | | |
| | | | 300 | 110—335 | | | |
| | | | 470 | 340—675 | | | |
| | | | 700 | 680—805 | | | |
| Manganese metavanadate | Mn -- 18.03% V -- 34.06% H ₂ O -- 12.48% | $Mn(VO_3)_2 \cdot 2H_2O$ | 815 | 805—830 | — | — | 12.4, within 110—335 °C |
| | | | 930 | — | | | |
| | | | 240 | 110—275 | | | |
| | | | 880 | 280—815 | | | |
| Silver orthovanadate | Ag -- 75.45% V -- 10.65% H ₂ O -- ml. | Ag_3VO_4 | 815—890 | 815—890 | — | — | 1.4, within 335—660 °C |
| | | | 180 | 110—225 | | | |
| | | | 455 | 415—500 | | | |
| | | | 640 | 620—650 | | | 9.587, within 110—275 °C |
| | | | | | | | 2.733, within 275—600 °C |
| | | | | | | | 0.508, within 110—225 °C |
| | | | | | | | 0.80, within 225—500 °C |

peak at 110–195° is significantly smaller than the 265° peak, which, in general, would indicate more water loss at the higher temperature. While the TG curve does not show a clear break under the experimental conditions, the break does appear at less than 10% and the subsequent plateau at 21–22%. This again indi-

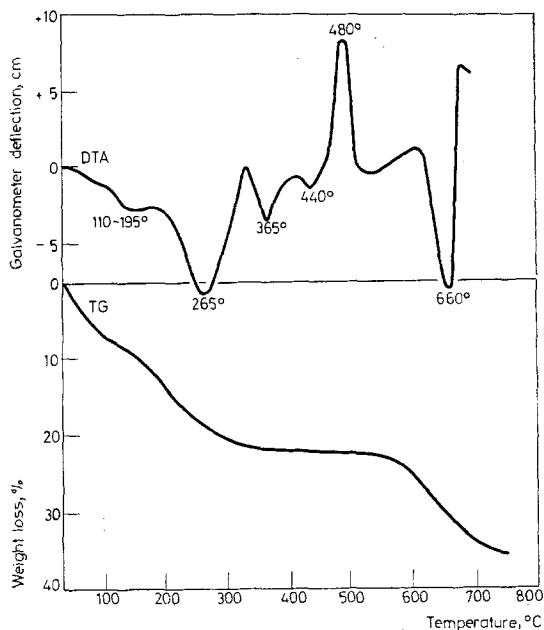


Fig. 1. DTA and TG curves of zinc pyrovanadate

cates more water loss in the second step i.e., a higher % of a smaller quantity. The TG curve did not record any weight-change within the temperature range 340–460° which reveals that the endothermic changes at 365° and 440° are not due to dehydration. The weight-loss registered in the TG curve even after 460° is not considerable up to 520°, which amounts to only 0.4%. Therefore, the exothermic change at 485° can be attributed to disorder-order transition (a process which does not accompany any weight-change of the substance). However, the weight-loss recorded within the range 610–675° is quite significant, amounting to 7.6% which suggests that the endothermic change at 660° is due to the decomposition of the pyrovanadate to some oxides of vanadium.

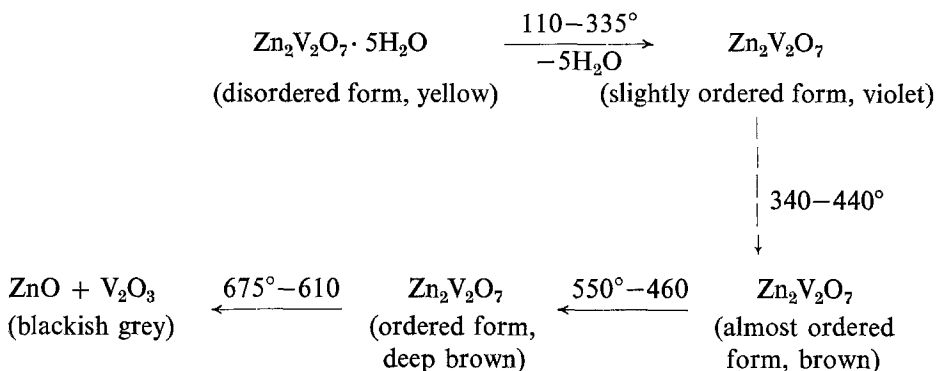
Infrared studies: The original catalyst sample displays in its IR spectrum a number of significant bands which can be assigned as follows: 3200 cm^{-1} band to H–O–H bending, 1140 and 1090 cm^{-1} bands to V–O–H bending, and 960 and 805 cm^{-1} bands to V–O stretching, characteristics of pyrovanadates. The spectrum of the 340° preheated sample offers the bands at 1010 and 860 cm^{-1} with the significant absence of the 960 and 805 cm^{-1} bands. This observation

reveals that even partial dehydration causes a change in structural characteristics of the catalyst. The catalyst appears to be completely dehydrated at 440° as the 440° preheated sample exhibits two strong bands at 1020 and 865 cm^{-1} instead of 1090, 960 and 805 cm^{-1} bands observed for the original one and the bands characteristic of water are absent. It is quite established that the metavanadates which contain both long and short types of VO bonds undergo structural changes during dehydration. The pyrovanadates in which VO bonds are of longer type, compared to metavanadates are not reported to undergo such type of changes so far. But it is evident from our studies that zinc pyrovanadate undergoes some basic structural changes during the course of dehydration. Therefore, the two bands at 1020 and 865 cm^{-1} can be assigned to the V—O stretching vibration of pyrovanadate, although these characteristic frequencies are reported for V—O stretching of V_2O_5 by Frederickson and Hauson [18].

The 550° preheated sample offers the relevant bands at 1060, 1020, 950 and 840 cm^{-1} which reveals that up to this temperature, the catalyst does not undergo any major change although 990 cm^{-1} band can be assigned to the V—O stretching of V_2O_3 in rough accord with Fredrickson et al. [18]. This characteristic band becomes more intense with the absence of 1020 and 840 cm^{-1} bands when the catalyst is heated at 710° suggesting the endothermic change at 660° to be due to decomposition of zinc pyrovanadate into zinc oxide and V_2O_3 . The conclusion gets substantiated by the registration of considerable weight-loss in the TG curve within the temperature range $610\text{--}675^\circ$ amounting to 7.6%.

X-ray diffraction (XRD) studies: X-ray analysis of the original catalyst sample exhibits a number of faint lines with a strong line at $d = 4.179\text{ \AA}$ indicating the crystal structure of the zinc pyrovanadate to be very near to amorphous state. The XRD patterns of the 340° preheated sample are almost the same as obtained earlier excepting that the d -values of few lines are shifted and the intensities of the lines are little enhanced. X-ray analysis reveals that the crystal structure of the catalyst heated at 440° is slightly ordered with the characteristic lines at $d = 3.491$ and 3.126 \AA . XRD patterns of the 550° preheated sample are little improved than the earlier ones with relevant line at $d = 3.042\text{ \AA}$ suggesting that the crystal structure of the pyrovanadate is almost ordered at this stage and the exothermic change at 485° is due to phase changes. X-ray diffraction studies do not indicate the decomposition of this zinc pyrovanadate at any stage of thermal treatment up to 550° .

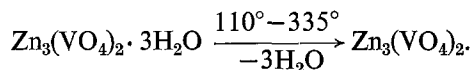
Magnetic susceptibility measurements: This study reveals that the original catalyst sample is diamagnetic of gram susceptibility 0.5512×10^{-6} . At higher temperatures, e.g. at 340° , this value is still less, whereas at 440° , it is 0.07015×10^{-5} . But at 550° , the catalyst is appreciably paramagnetic of gram susceptibility 4.422×10^{-6} , whereas at 710° , this value is 17.62×10^{-62} . These observations clearly indicate that the endothermic change at 660° may be responsible for this abrupt increase of paramagnetic susceptibility and the formation of V_2O_3 is quite likely at this stage. Therefore, the thermal changes in zinc pyrovanadate can be expressed as follows:



As it appears from literature survey that zinc pyrovanadate is fairly active at 450° for many reactions [3], it can be suggested from our studies that it is the relatively amorphous state of this catalyst which acts as the vehicle of catalytic activity. As this catalyst undergoes crystallization (which is detrimental to catalytic activity) beyond 460° and complete dehydration at 335°, it is very reasonable to conclude that zinc pyrovanadate should be catalytically active within the temperature range 335–460° and it would appear activity would be associated with disorder.

Zinc orthovanadate

Thermal analysis: DTA and TG curves of this catalyst are shown in Fig. 2. The DTA curve shows a sharp endothermic peak at 300° followed by a flat endothermic change at 340–675° and two successive endothermic peaks at 700°, 815° and one exothermic spike near 815° and the last endothermic peak at 930°. The TG curve registers a total weight-loss amounting to 13.81% within 110–660°. A well defined plateau is observed in TG curve within 110–335° suggesting the dehydration course to proceed through single step reaction. However, the weight-loss recorded within this temperature range amounts to 11.50% which corresponds to the removal of almost three molecules of water from one molecule of $\text{Zn}_3(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$. Therefore, the endothermic change at 300° is clearly due to the following reaction:



There appears a very weak endothermic peak at 470° in the DTA curve which on projection to the TG curve is seen to follow a less well defined plateau suggesting this peak to be due to the removal of strongly adsorbed trace of water from the compound. There is, however, no substantial weight-change registered in the TG curve within the range 480–700°.

Infrared studies: The characteristic band observed in the spectrum of the original catalyst sample are at 925 and 805 cm^{-1} which are assigned to the V–O stretching

in addition to a number of bands representing different modes of water. The bands corresponding to water of crystallization are still present in the spectrum of the 340° preheated sample although too weak with the significant missing of the 925 cm^{-1} band. This change is simply due to dehydration. The 580° preheated sample offers the relevant bands at 905 , 860 and 800 cm^{-1} which are indicative of V–O stretching (as in the case of orthovanadates) and the substance appears to be almost dehydrated. The original crystal structure is observed to undergo appreciable

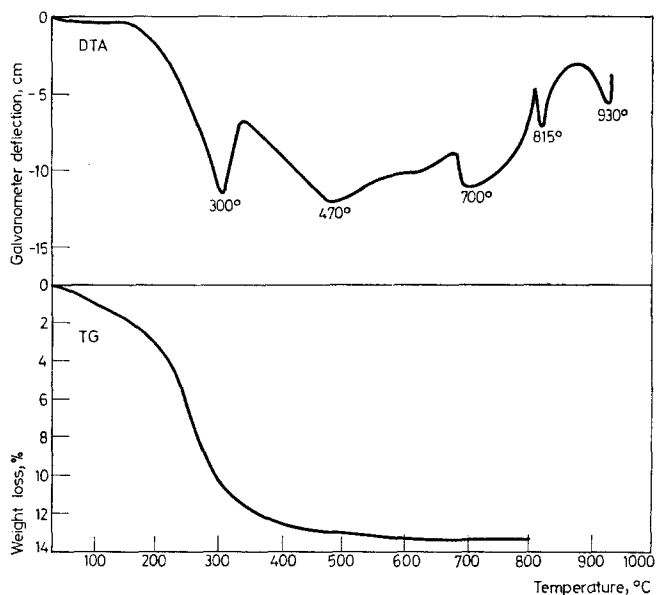


Fig. 2. DTA and TG curves of zinc orthovanadate

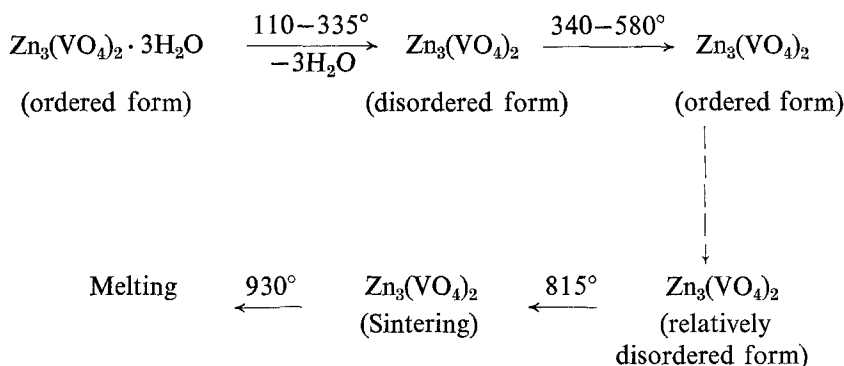
transformation at 770° as the sample preheated at this temperature displays its spectrum very weak bands in the characteristic region $920-725\text{ cm}^{-1}$. However, the 1000° preheated sample offer all the bands at 920 , 870 and 780 cm^{-1} which are characteristic of V–O stretching (as observed in the case of $(\text{VO}_4)^{3-}$) indicating thereby the retention of original orthovanadate character even at this very high temperature.

X-ray diffraction studies: X-ray analysis of the original catalyst sample shows a well defined diffraction pattern indicating the crystal structure of the compound to be crystalline (characteristic lines are at $d = 7.291$, 3.000 , 2.659 , 2.505 \AA etc.). XRD patterns of the 340° preheated sample are entirely different than those obtained earlier. The few faint lines appear at $d = 2.575$, 2.115 and 1.492 \AA . The crystal structure of the compound is reasonably disordered at this temperature. Therefore, it is apparent that dehydration causes a substantial structural change of the catalyst molecule. XRD patterns of the 580° preheated sample are

even more distinct and well defined than observed in the case of original catalyst sample. The crystal structure of the compound seems to be completely ordered at this stage. The characteristic lines are seen at $d = 3.042, 2.575, 2.477, 2.086, 1.470 \text{ \AA}$ etc. Therefore, the endothermic changes within $340-580^\circ$ are due to phase changes. XRD patterns of the sample heated at 770° are not similar to those obtained in the just preceding case as very less number of lines appear in the diffraction pattern with low intensity. The crystal structure of zinc orthovanadate seems to be relatively disordered at this stage ensuring the endothermic change at 700° to be due to order-disorder transition. X-ray analysis, however, does not indicate the decomposition of zinc orthovanadate into its component oxides at any stage of thermal treatment.

Magnetic susceptibility measurements: This study indicates that zinc orthovanadate is feebly paramagnetic of gram susceptibility 1.240×10^{-6} and at higher temperature of calcination, this value remains almost unchanged.

Therefore, the thermal changes in zinc orthovanadate can be summed up as follows:



Literature survey reveals that zinc orthovanadate is catalytically active within the temperature range $250-450^\circ$. It is very clear from the structural studies of this catalyst that order-disorder transitions are the determining factor for catalytic activity.

Manganese metavanadate

Thermal analysis: DTA and TG curves of this catalyst are shown in Fig. 3. The DTA curve shows one sharp endothermic peak at 240° followed by a long flat endothermic peak at $280-815^\circ$. Again there appears a very poor exothermic dent at 515° followed by an endothermic change at 880° . The TG curve records a total weight-loss amounting to 12.32% within $110-600^\circ$ which corresponds to the removal of two molecules of water from one molecule of $\text{Mn}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$. The continuous weight-loss registered in the TG curve within $110-275^\circ$ amounts to 9.5% which corresponds to the removal of one and a half molecules of water from one molecule of $\text{Mn}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$. At 600° , the weight loss is in excess of

12% and accelerating. There is definitely a transition in rate loss between 275 and 600° which could be two-step loss.

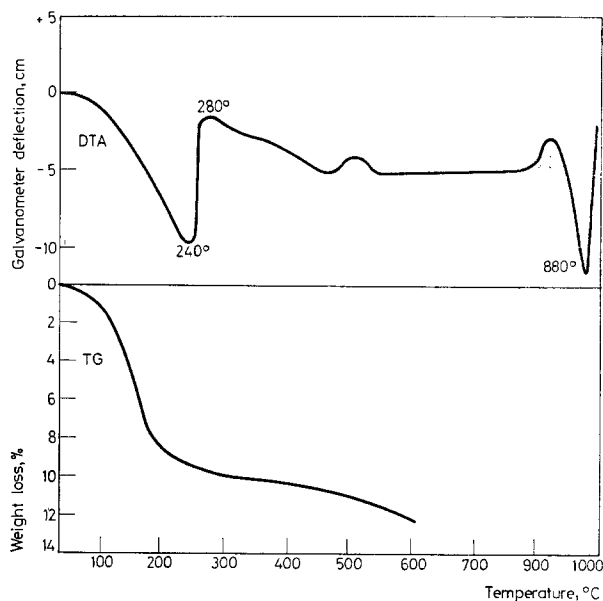
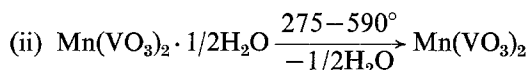
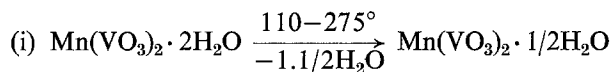


Fig. 3. DTA and TG curves of manganese metavanadate

Infrared studies: In addition to the bands characteristics of O–H stretching, H–O–H bending and V–O–H bending, the spectrum of the original catalyst sample offer the bands at 970 and 830 cm^{-1} which are assigned to the V–O stretching, as in the case of metavanadates [18]. At 280°, the compound appears to be almost dehydrated which is revealed by the absence of bands characteristic of water as well as presence of a single strong band at 850 cm^{-1} . The catalyst does not undergo any appreciable change within 280–590°. However, two significant bands although weak, are noticed at 1020 and 830 cm^{-1} in the spectrum of the 830° preheated sample which can be assigned the V–O stretching as in the case of V_2O_5 . Therefore, the endothermic behaviour beyond 590° can be attributed to slow decomposition.

X-ray diffraction studies: X-ray analysis of the original catalyst sample exhibits a diffused diffraction pattern with characteristic lines at $d = 6.525$ and 3.193 Å

prepared by the method reported by Bhattacharyya et al. [1] were also carried out. DTA curve of AgVO_3 indicates that silver metavanadate does not undergo any thermal change when heated up to 450° . These two vanadates of silver exhibit almost similar TG curves with minor difference in the DTA curve.

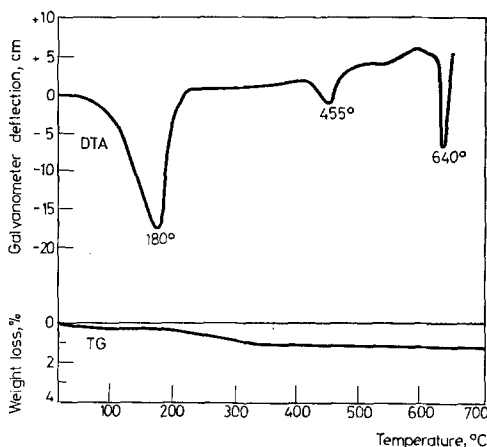


Fig. 4. DTA and TG curves of silver orthovanadate

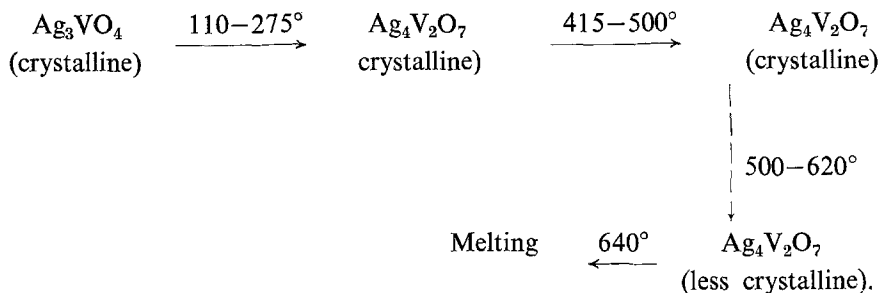
Infrared studies: The spectrum of the original catalyst sample displays two very weak bands at 3330 and 1150 cm^{-1} characteristic of loosely held water and one very strong band at 735 cm^{-1} which is assigned to the V—O stretching vibration. The 265° preheated sample offers almost all the same bands with the shifting of 735 cm^{-1} . However, the samples heated at 380° and 510° exhibit in their spectra a very weak broad band at 730 cm^{-1} . This change in intensity of the band may be due to complete removal of moisture. The 620° preheated sample does not indicate any considerable change in its spectrum excepting a little shifting of the weak 730 cm^{-1} band to 720 cm^{-1} . It is very clear from the IR studies that the characteristic strong band of the original sample undergoes severe changes in course of thermal treatment and that band no longer exists at higher temperatures.

IR studies of silver metavanadate heated at 350° reveal the presence of a very weak band at 1600 cm^{-1} and a number of strong bands at 840 , 890 , 920 and 960 cm^{-1} . The latter bands are indicative of V—O stretching motion as observed in the case of metavanadates [1, 18]. IR spectral studies of silver metavanadate reveal that this catalyst undergoes no thermal change before fusion whereas silver orthovanadate seems to undergo some changes on thermal treatment.

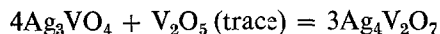
X-ray diffraction studies: X-ray analysis of the original catalyst sample exhibits a distinct diffraction pattern with the well defined lines at $d = 4.6$, 2.87 , 2.75 , 2.55 , 2.48 , 1.69 \AA etc. revealing the crystal structure of the original catalyst to be crystalline. These d -values compare excellently to those reported for standard patterns

of both- silver orthovanadate and silver pyrovanadate $\text{Ag}_4\text{V}_2\text{O}_7$ (A. S. T. M. Card, 1-0946). XRD patterns of 260° , 380° and 510° preheated samples are almost the same as obtained earlier with the relevant lines at $d = 4.6, 2.88, 2.76, 2.17, 1.78, 1.77 \text{ \AA}$ etc. It is thus very clear that beyond 260° the catalyst is no longer orthovanadate (Ag_3VO_4) but purely silver pyrovanadate $\text{Ag}_4\text{V}_2\text{O}_7$. However, the XRD patterns of the sample heated at 620° are little changed than earlier as is indicated by the presence of new lines at $d = 3.48, 2.79, 2.7, 2.13$ as well as missing of the lines at $d = 2.17, 1.78, 1.77 \text{ \AA}$ etc., although all the characteristic lines are retained at this stage.

X-ray diffraction studies of silver metavanadate indicate that this catalyst does not undergo any structural change before fusion although minute traces of Ag, AgO, V_2O_5 etc. could be detected in the silver metavanadate when heated at 350° . This observation is substantiated by very small oxygen chemisorption of this catalyst which is due to the minute traces of V_2O_5 , present in it. Therefore the thermal changes in silver orthovanadate can be summed up as follows:



However, the presence of minute traces of V_2O_5 on the silver orthovanadate could not be ruled out when heated around 275° . This may be the reason for the transformation of orthovanadate into the pyrovanadate in the following way:



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RÉSUMÉ — On a étudié par ATD et TG les caractéristiques thermiques des vanadates de zinc, de manganèse et d'argent. La caractérisation des divers produits de transition ainsi obtenus a été effectuée à partir des données fournies par IR, rayons X et susceptibilité magnétique. Les analyses chimiques indiquent les compositions suivantes de ces vanadates: (1) $Zn_2V_2O_7 \cdot 5H_2O$, (2) $Zn_3(VO_4)_2 \cdot 3H_2O$, (3) $Mn(VO_3)_2 \cdot 2H_2O$ et (4) Ag_3VO_4 . Les courbes ATD du pyrovanadate de zinc montrent des effets endothermiques à 110–195, 265, 365, 440 et 660° ainsi qu'un phénomène exothermique à 485°. Ce corps est diamagnétique; il devient complètement paramagnétique au-dessus de 660°. L'orthovanadate de zinc donne des pics endothermiques à 300, 470, 700, 815 et 930°. Il est faiblement paramagnétique jusqu'à 930°. Le métavanadate de manganèse est le siège de phénomènes endothermiques à 240, 280–590, 830 et 880°. Il est paramagnétique et son paramagnétisme augmente de manière appréciable à 590° pour rester constant jusqu'à 830°. L'orthovanadate d'argent montre trois effets endothermiques à 180, 455 et 640°.

ZUSAMMENFASSUNG — Die thermischen Charakteristika der Vanadate von Zink, Mangan und Silber wurden durch DTA- und TG-Methoden untersucht und die auf diese Weise erhaltenen verschiedenen Übergangsprodukte durch Daten aus IR-, Röntgen- und magnetischer Suszeptibilität charakterisiert. Die chemische Analyse deutet auf folgende Zusammensetzung dieser Vanadate: 1) $Zn_2V_2O_7 \cdot 5H_2O$, 2) $Zn_3(VO_4)_2 \cdot 3H_2O$, 3) $Mn(VO_3)_2 \cdot 2H_2O$ und 4) Ag_3VO_4 . Die DTA-Kurven zeigen endotherme Veränderungen des Zink-pyrovanadats bei 110–195, 265, 365, 440 und 660° und eine exotherme Veränderung bei 485°. Dieses System ist diamagnetisch und wird nach 660° vollständig paramagnetisch. Zink-orthovanadat zeigt eine Anzahl exothermer Peaks bei 300, 470, 700, 815, bzw. 930°. Dieses System ist schwach paramagnetisch und behält diese Eigenschaft bis zu 930°. Im Manganmetavanadat vollziehen sich endotherme Veränderungen bei 240, 280–590, 830 und 880°. Dieses Vanadat ist paramagnetisch, der Paramagnetismus steigt zusehends bei 590° und bleibt bis zu 830° konstant. Silberorthovanadat zeigt drei endotherme Veränderungen bei 180, 455 bzw. 640°.

Резюме — Были изучены с помощью ДТА и ТГ термические характеристики ванадатов цинка, марганца и серебра. Полученные при этом переходные продукты были охарактеризованы с помощью ИК-спектроскопии, рентгеноструктурного анализа и данных по магнитной восприимчивости. Данные химического анализа указывают на следующий состав этих ванадатов: $Zn_2V_2O_7 \cdot 5H_2O$, $Zn_3(VO_4) \cdot 3H_2O$, $Mn(VO_3)_2 \cdot 2H_2O$ и Ag_3VO_4 . Кривые ДТА показывают, что пированадат цинка подвергается эндотермическим изменениям при $110-195^\circ$, 265 , 365 , 440 и 660° и одному экзотермическому изменению при 485° . Эта система является диамагнитной, которая после 660° становится полностью парамагнитной. Ортованадат цинка показывает ряд эндотермических пиков соответственно при 300 , 470 , 700 , 815 и 930° . Эта система проявляет слабые парамагнитные свойства и сохраняет их до 930° . Метаванадат марганца подвергается эндотермическим изменениям соответственно при 240 , $280-590$, 830 и 880° . Этот ванадат обладает парамагнетизмом, который заметно усиливается при 590° и остается постоянным до 830° . Ортованадат серебра проявляет эндотермические пики при 180 , 455 и 640° .