

Physico-chemical Properties of Bismuth Pyrovanadate Catalyst

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Thermal behaviour of bismuth pyrovanadate ($\text{Bi}_4\text{V}_6\text{O}_{21} \cdot 6\frac{1}{2}\text{H}_2\text{O} \cdot 1\frac{1}{2}\text{NH}_3$) has been studied and the various transition products have been characterized by chemical analysis, IR, X-ray diffraction, surface area (BET) and magnetic susceptibility techniques. The vanadate undergoes endothermic changes at 110-260° (flat), 420-600° (flat), 665° and 928°. The endothermic changes up to 260° are due to stepwise dehydration, at 420-600° are for slow decomposition of adsorbed impurities, at 665° on account of partial decomposition of the vanadate and at 928° are due to melting. The exothermic changes are due to stepwise disorder-order transitions. The fresh compound is amorphous. All the samples, fresh as well as treated ones, are diamagnetic. The vanadate displays maximum surface area as well as disordered structure ($\sim 290^\circ$) corresponding to complete dehydration.

It has been reported that the optimum temperature range for catalytic activity of bismuth vanadates, widely used catalysts for oxidation of aromatic hydrocarbons and other reaction¹⁻⁶, is dependent on the nature of reaction as well as on their mode of preparation. For example, the active temperature ranges for oxidation of a number of systems are as follows: furan derivatives (290-320°)³, isobutene (400°)⁴, xylenes (380-90°)⁵ and propylene (500°)⁶. As the physico-chemical properties of a catalyst are of direct significance in relation to its activity it was thought worth while to study some of the structural aspects of a model bismuth pyrovanadate employing differential thermal analysis (DTA), thermogravimetry (TG), infrared, X-ray diffraction, magnetic susceptibility and surface area of bismuth pyrovanadate as well as of its thermal transition products.

Materials and Methods

Preparation of catalyst—A warm (60°) 0.25M solution of bismuth nitrate (48.5 g/400 ml water), acidified with nitric acid to pH 3, was added slowly (50 ml at a time) by stirring to 1M ammonium metavanadate solution (34.9 g/300 ml water) followed by digestion of the final mixture (pH 6) for 45 min at 90°. The substance was allowed to settle, filtered, washed repeatedly with hot water until free from adsorbed soluble impurities and dried in an air-oven at 110° for 24 hr.

Bi^{3+} was analysed by precipitation of Bi_2S_3 by H_2S in acidic solution followed by ignition and weighing as Bi_2O_3 . V^{5+} in solution was analysed by redox titration with Mohr's salt in H_2SO_4 using diphenylamine-phosphoric acid indicator. The amount of water was determined using Coleman carbon-hydrogen analyser and ammonia by Coleman nitrogen analyser.

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Thermal analysis—Differential thermal analysis (DTA) was carried out in air as well as in a nitrogen atmosphere, using a manually-operated DTA apparatus⁷. The sample holder was a cylindrical nickel block with two holes of 0.86 cm diameter each. $\alpha\text{-Al}_2\text{O}_3$ served as a reference material. Sample weight was ~ 500 mg. Thermogravimetric (TG) analysis was carried out in a Stanton mass flow thermobalance, model MFH-5, with a programmed heating rate of 6.5°/min in an air atmosphere with sample weight of ~ 100 mg.

Preparation of Bi vanadate samples—The samples were prepared by heating the Bi vanadate at the following temperatures for 2 hr in each case: 140°, 260°, 310°, 400°, 600° and 720°.

Infrared studies—IR spectra of the above samples were taken in nujol medium using a grating infrared spectrophotometer (Perkin-Elmer model 257).

X-ray diffraction studies—X-ray diffraction patterns of all the samples were obtained using a Philips diffractometer with nickel-filtered CuK_α radiation. The setting was the same as described earlier⁷.

Surface area measurements—Surface areas of some of the samples were determined by low temperature nitrogen adsorption BET method.

Magnetic susceptibility measurements—Magnetic susceptibilities of all the samples were determined by Faraday method at 300°K using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as calibrant.

Results and Discussion

The catalyst analysed for $\text{Bi}_4\text{V}_6\text{O}_{21} \cdot 6\frac{1}{2}\text{H}_2\text{O} \cdot 1\frac{1}{2}\text{NH}_3$ (Bi, 53.26; V, 19.16; H_2O , 6.8; NH_3 , 1.5%). DTA and TG curves of this vanadate are shown in Fig. 1. DTA curve shows that the system undergoes endothermic (endo-) changes at 110-260° (flat), 420-60° (flat), 665° and 928° and exothermic (exo-) changes at 305° and 390°C. In nitrogen atmosphere endo-peaks are observed at 225°, 510°, 745° and exo-peaks at 325° and 460°C. TG curve indicates 6.205% weight loss within 130-260° and 1.20%

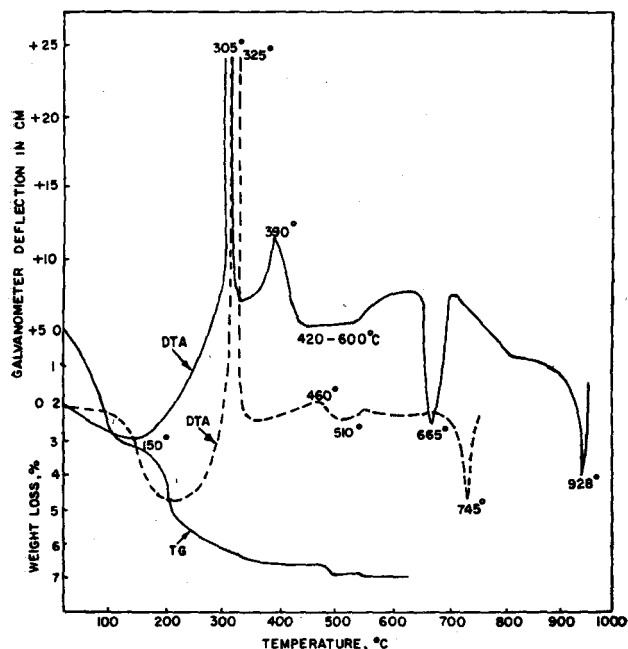


Fig. 1 — DTA and TG of bismuth pyrovanadate

within 290-310°. TG results reveal that the endo-change at 110-260° is due to partial dehydration and the subsequent weight loss may be due to complete dehydration. The insignificant weight loss after 300° suggests the exo-changes to be due to phase changes. The same inference is supplemented by retention of all the exo-peaks in nitrogen atmosphere.

IR spectral data of all the samples given in Table 1 show bands in the region 950-720 cm^{-1} , assigned to the $\nu\text{V-O}$ as observed in the case of polyvanadates⁸. The other bands in the region 3500-3200, 2350-2300 cm^{-1} are assigned $\nu\text{O-H}$ stretching and those at 1625-1580 and 1150-1130 cm^{-1} are attributed to H-O-H and V-O-H bending respectively⁹. The $\nu\text{V-O}$ observed at two distinct regions 900-1000 and 720-780 cm^{-1} indicate that there is one short VO bond at each vanadium atom with the remaining VO bonds being appreciably longer and more variable. Thus, vanadium in this system may coordinate with either five or six oxygens, existing in the form of zigzag chains of VO_6 octahedra, joined at centres to form corrugated sheets or layered structures. It is evident from Table 1 that vanadate is completely dehydrated at a temperature less than 310°. Thus, the

TABLE 1 — IR SPECTRAL DATA (cm^{-1}) OF BISMUTH VANADATE SAMPLES

Bv 2/3 110:	3420 mb, 3200 mb, 2300 vv, 1620 mb, 1150 vv, 950 vv, 775 sb
Bv 2/3 140:	3420 mb, 3200 mb, 1625 m sh, 1150 vv, 945 vv, 895 wsh, 780 sb
Bv 2/3 260:	3500 mb, 1625 msh, 960 vv, 770 mb
Bv 2/3 310:	1005 sb, 830 vv
Bv 2/3 400:	1010 ssh, 830 mb
Bv 2/3 600:	1320 wsh, 1150 wsh, 1010 ssh, 800 vv
Bv 2/3 720:	1320 wsh, 1150 wsh, 1025 wsh, 1010 mb, 800 vv

Bv 2/3 110 signifies Bi vanadate of Bi/v ratio 2/3 calcined at 110°C for 2 hr in air.

TABLE 2 — RESULTS OF X-RAY ANALYSIS OF BISMUTH VANADATE (2/3) HEATED AT DIFFERENT TEMPERATURES

d (Å)	I/I_1	d (Å)	I/I_1	d (Å)	I/I_1	d (Å)	I/I_1	d (Å)	I/I_1
Bv 2/3 110*		Bv 2/3 310		Bv 2/3 400		Bv 2/3 600		Bv 2/3 720	
Bv 2/3 140		6.726	vvw	5.837	vvw	5.837	vvw	5.837	vvw
		4.762	ms	4.762	s	5.333	vvw	4.552	ms
6.525	vvw	4.387	vw	4.520	w	5.032	vvw	4.387	vs
5.543	vvw	3.755	w	4.387	m	4.762	ms	4.102	ms
5.333	vvw	3.465	vvw	3.819	vw	4.387	ms	3.922	vw
4.762	vvw	3.177	vs	3.724	mw	4.102	vw	3.465	vw
3.755	vw	2.923	ms	3.412	mw	3.412	vw	3.216	vw
2.282	vw	2.547	ms	3.177	vs	3.216	vw	3.155	vs
		2.375	ms	2.923	ms	3.083	vs	2.923	vs
Bv 2/3 260		2.124	m	2.746	w	2.923	ms	2.651	ms
		2.069	mw	2.651	ms	2.651	ms	2.533	ms
6.829	vvw	1.973	ms	2.533	ms	2.547	ms	2.238	ms
4.762	vvw	1.933	s	2.464	vvw	2.249	ms	2.175	s
3.922	vvw	1.809	ms	2.312	s	2.175	vvw	2.124	ms
3.177	ms	1.713	s	2.116	ms	2.115	ms	2.050	m
3.024	vvw	1.639	vw	2.069	vw	1.973	ms	1.933	m
2.651	vw	1.596	ms	1.973	mw	1.933	m	1.910	ms
2.339	vvw			1.933	ms	1.910	ms	1.806	m
2.324	mw			1.918	ms	1.809	ms	1.778	vvw
2.124	mw			1.809	ms	1.707	s	1.707	s
2.024	vvw			1.769	mw	1.639	vw	1.639	m
1.973	vw			1.707	s	1.571	ms	1.571	ms
1.918	mw			1.677	vvw	1.542	ms	1.561	ms
1.858	vw			1.639	mw			1.449	m
1.806	mw			1.571	m			1.263	m
1.713	m			1.542	ms			1.248	m

I/I_1 = visually estimated intensity; vs = very strong; s = strong; ms = medium strong; m = medium; mw = medium weak; w = weak; vw = very weak; vvw = very very weak.

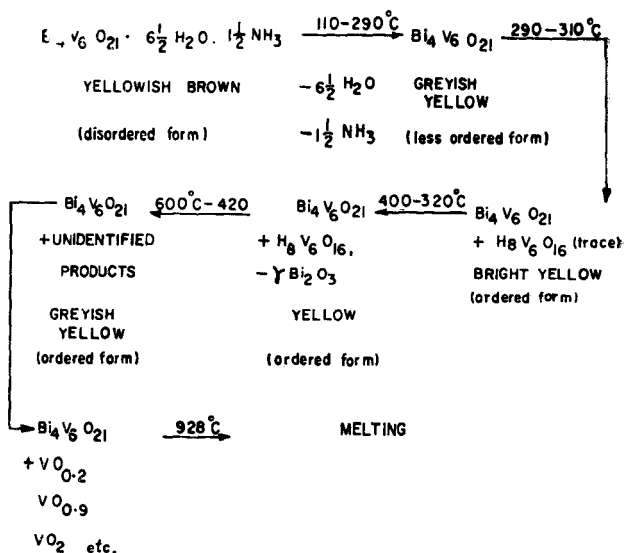
*Bv 2/3 110 signifies Bi vanadate of Bi/v ratio 2/3 calcined at 110° for 2 hr in air.

endo-changes prior to exo- ones are due to stepwise dehydration. The band at 1005 cm^{-1} of the sample Bv 2/3 310 may be due to the presence of excess ammonium metavanadate in the catalyst (which could not be removed even by repeated washing with hot water). However, 1025 cm^{-1} band of the sample Bv 2/3 720 is due to $\nu\text{V-O}$ stretching of V_2O_5 or lower valent oxides⁸. A little shift of the common bands of all the samples is suggested to be due to removal of oxygen at higher temperatures.

The results of X-ray analysis of various bismuth vanadate samples are shown in Table 2. The fresh catalyst, i.e. Bv 2/3 110, is amorphous. Endo-changes are found not to affect the crystal structure of this vanadate. It may be due to the large rigid framework of polyvanadate that hardly changes due to expulsion of a few loosely held water molecules during dehydration. However, at the temperature at which the exo-peaks appear in TG, the crystal structure becomes slightly ordered. It indicates that on heating, the reversion from disordered state to ordered state takes place with evolution of thermal energy. Thus, the exo-changes at 305° and 390° are due to stepwise disorder-order transitions. This conclusion is supplemented by the record of negligible weight loss in the TG curve in this temperature range as well as by the retention of the exo-peaks in nitrogen atmosphere. Smolyaninov *et al.*¹⁰ already reported about the phase transition of $\text{Bi}_4(\text{V}_2\text{O}_7)_3$ at $200\text{--}280^\circ$ and decomposition at 720° . Thus, the assignment of exo-changes by disorder-order transitions is justified. Levy¹¹ also observed that BiVO_x , $\text{Bi}_4\text{V}_3\text{O}_x$, etc., undergo phase transformation with the formation of a new phase on being thermally heated. Other workers^{12,13} also observed that BiVO_4 (orthorhombic) was converted to the monoclinic form by prolonged heating at 500° . X-ray analysis of Bv 2/3 400 indicates the presence of $\text{H}_8\text{V}_6\text{O}_{16}$ and $\gamma\text{-Bi}_2\text{O}_3$ ($d = 3.177, 2.651, 1.707\text{ \AA}$ which may account for the presence of excess ammonium metavanadate and $\text{Bi}(\text{OH})_3$ in the fresh sample. X-ray diffraction pattern of Bv 2/3 600 does not indicate the presence of $\text{H}_8\text{V}_6\text{O}_{16}$ whereas the same of Bv 2/3 720 reveals the presence of $\text{VO}_{0.2}$, $\text{VO}_{0.9}$, VO_2 , etc. Thus, the sharp endo-change at 665° may be due to decomposition of $\text{H}_8\text{V}_6\text{O}_{16}$ as well as partial decomposition of bi vanadate. In nitrogen atmosphere this endo-peak is observed $\sim 710\text{--}60^\circ$ which reasonably matches with the temperature of decomposition as reported earlier¹⁰.

All the bi vanadate samples are diamagnetic. The various colour centres developed in course of thermal treatment may thus be due to reorganization of the defects or dislocations which are typical in this class of catalysts.

Surface areas of some of the bi vanadate samples are as follows: Bv 2/3 260-23.5 m^2/g ; Bv 2/3



Scheme 1 — Products formed at the various stages of thermal treatment of bismuth pyrovanadate

290-30.61 m^2/g ; Bv 2/3 310-29.50 m^2/g ; Bv 2/3 400-9.8 m^2/g ; and Bv 2/3 500-36.8 m^2/g .

These data indicate that bi vanadate is not completely dehydrated at 260° and the completely anhydrous state may be somewhere in the region $260\text{--}290^\circ$. The maximum surface area corresponds to complete dehydration and the surface area gets reduced stepwise due to a series of disorder-order transitions. The higher surface area at 500° may be due to the lower valent oxides of vanadium formed by slow decomposition of $\text{H}_8\text{V}_6\text{O}_{16}$ at that temperature.

Summarizing all the data, the thermal changes of the bi vanadate (2/3) can be expressed as shown in Scheme 1.

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