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STUDIES ON THERMAL PROPERTIES OF BISMUTH VANADATE CATALYSTS

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Physicochemical properties of bismuth vanadate catalysts with varying compositions, e.g., $Bi_4V_6O_{21} \cdot 6\frac{1}{2}H_2O \cdot 1\frac{1}{2}NH_3$; $Bi_6V_2O_{14} \cdot 3\ H_2O$; $Bi_6V_4O_{19} \cdot 6\ H_2O$ have been studied by chemical analysis, differential thermal analysis, thermogravimetry, infrared, X-ray diffraction, surface area and magnetic susceptibility techniques.

The endotherms, in all the cases, prior to exo ones are due to stepwise dehydration and those following exochanges are due to decomposition of adsorbed impurities, sintering and melting, etc. The last endopeak, in all the cases, however is due to melting. The exochanges are attributed to stepwise phase transitions. The V – 0 stretching in all the compounds is characteristic of polyvanadates. Two types of vanadium-oxygen bonds e.g., V = O and V – O – V are characterized by IR analysis. The fresh first and third vanadates are amorphous whereas the second one is crystalline. The exochanges (presumably due to disorder-order transitions) are suggested to be related to displacement of oxygen anions. The precipitated vanadates are similar with their corresponding solid state reaction products of Bi_2O_3 and V_2O_5 when they are heated at elevated temperature. The fresh as well as treated vanadates are diamagnetic. These systems display maximum surface area at the temperature corresponding to complete dehydration. The composition of the precipitated vanadates is not ultimately defined by Bi/V ratio and the binary compound consequently formed.

Oxides of vanadium, molybdenum, and related elements find frequent use as oxidation catalysts. The application of V_2O_5 for the oxidation of aromatics has been known for a considerable time: the oxidation of naphthalene and o-xylene to phthalic anhydride and of benzene to maleic anhydride have been applied in the industry for some decades. Somewhat more recent is the discovery of the selective oxidation of olefins.

Maxted an Coke [1 – 3] reported on the oxidation of a number of aromatic hydrocarbons over bismuth vanadate (BV) catalysts while Milas and Walsh [4] worked on the oxidation of furan derivatives. Stamicarbon observed that these type of catalysts were quite active for oxidation of isobutene at 400° [5] and of propylene at 500° [6]. Literature on the physicochemical properties of BV catalysts is meagre. According to Levy [7] $BiVO_x$, $Bi_4V_3O_x$, etc. undergo the formation of a new phase on being thermally treated. Smolyaninov and Belyaev [8] studied

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the ternary system $Bi_2O_3-V_2O_5-PbO$. In the $Bi_2O_3-V_2O_5$ range they found the following compounds: 7 $Bi_2O_3-V_2O_5$, *m.p.* 955°; $BiVO_4$, *m.p.* 958°, phase transitions at 200–250°; $Bi_4(V_2O_7)_3$, decomposition temp. 830°, phase transitions at 200–280°; $Bi(VO_3)_3$, decomposition temp. 720°, phase transitions at 200–280°. Quarashi *et al.* [9] reported that $BiVO_4$ is orthorhombic with $a = 5.33$, $b = 5.06$, $c = 12.2$ Å; $Z = 4$, Space group Pnea. Roth *et al.* [10] observed that orthorhombic $BiVO_4$ was converted to the monoclinic form by prolonged heating at 500°. Literature survey reveals that bismuth vandates are catalytically active within the temperature range 290–500° [1–6]. Thus, it appears that the catalytic actions of these catalysts are related to their thermal characteristics. No systematic investigations on the thermal properties of BV have been reported so far. The present study was undertaken in order to obtain information on the physicochemical properties of BV with varying compositions using differential thermal analysis (DTA), thermogravimetry (TG), infrared (IR) spectroscopy, X-ray diffraction (XRD), surface area (BET) and magnetic susceptibility techniques.

Experimental

Preparation of the catalysts

The bismuth vanadates of varying compositions have been prepared by coprecipitation method by adding ammonium metavanadate to bismuth nitrate in solution. The choice of precipitation conditions was determined by the following criteria:

Table 1

Preparation of Bi-vanadate catalysts

Catalyst	Bismuth nitrate soln. aicidified with nitric acid, g/ml of water (A)	Ammonium metavanadate soln. g/ml of water (B)	Mode of addition; ml at a time (A) → (B)	pH of the final mixture	Chemical formula	Composition
BV 2/3	48.5/400	34.9/300	50	6.0–7.0	$Bi_4V_6O_{21} \cdot 6\frac{1}{2}\ H_2O \cdot 1\frac{1}{2}\ NH_3$	Bi–53.26, V–19.16 H_2O–6.8, NH_3–1.5
BV 3/1	19.4/400	34.9/300	25	6.0–6.5	$Bi_6V_2O_{14} \cdot \cdot 3\ H_2O$	Bi–76.72, V–6.24 H_2O–3.33
BV 3/2	33.96/300	1.17/50	20	6.0–7.0	$Bi_6V_4O_{19} \cdot \cdot 6\ H_2O$	Bi–65.67, V– –10.92 H_2O–6.03

[1] BV 2/3 signifies bismuth vanadate of Bi/V ratio, 2/3

[2] In all the cases, the pH of the final mixture was maintained by adding ammonia solution and the precipitates were digested for 45 min. at 60°. Then they were allowed to settle, filtered off and washed with hot water and ultimately dried in an air-oven at 110° for 24 hr.

(i) Evaporation of the solution was avoided in order to prevent precipitation of pure hydroxides

(ii) Precipitation pH was kept low in order to avoid precipitation of $Bi(OH)_3$ and

(iii) Control of the degrees of polymerisation of V anions was made by adjustment of pH, temperature of precipitation and concentration of vanadium and bismuth ions. The details of the preparation of all the vanadates are summarized in Table 1.

Chemical analysis of the catalysts

Vanadium: V^{5+} in solution was analyzed by redox titration with Mohr's salt in H_2SO_4 using diphenylamine-phosphoric acid indicator. Bismuth: Bi^{3+} in solution was analyzed as Bi_2O_3 by precipitation with H_2S in acidic solution and calcination at 500°.

Water and ammonia*:* These contents were determined using Coleman nitrogen, carbon, hydrogen Analyser.

Physicochemical properties of the catalysts

DTA of all the vanadates were carried out in air as well as in nitrogen atmosphere, using a manually-operated DTA apparatus [11]. The sample holder was a cylindrical nickel block with two holes of 0.86 cm diameter each. α-Al_2O_3 served as a reference material. Sample weight was 500 mg in all the cases. TG of all the systems were carried out in a Stanton Mass Flow Thermobalance, Model MFH-5, with a programmed heating rate of 6.5° min in air. Sample weight was 100 mg in each case XRD patterns of all thevanadates obtained using a Philips diffractometer with nickel-filtered CuK_α radition. The setting was the same as described in ref. [11].

IR spectra of all the samples were taken in nujol medium using a grating infrared spectrophotometer (Perkin – Elmer Model 257). Surface area of all the samples was determined by low temperature nitrogen adsorption BET method.

Gram susceptibilities (x_g) of all the samples were determined by Faraday method at 300 K using $Hg[Co(NCS)_4]$ as calibrant.

Preparation of the samples

The samples were prepared by calcination of the vanadates at the following DTA transition temperatures in air for 2 hr in each case.

Bismuth vanadate (Bi/V = 2/3): 110°, 140°, 260°, 310°, 400°, 600°, 720°
or (BV 2/3)
Bismuth vanadate (Bi/V = 3/1): 110°, 210°, 320°, 370°, 570°, 630°
or (BV 3/1)
Bismuth vanadate (Bi/V = 3/2): 110°, 190°, 300°, 400°, 530°
or (BV 3/2)

A fused bismuth vanadate sample was prepared by igniting a mixture of Bi_2O_3 and V_2O_5 (ratio, 2/3) at 600° in air for 8 hr.

Results and discussion

Bismuth Vanadate (2/3) or BV 2/3

Preparation and chemical analysis

The composition of this vanadate is established as $Bi_4V_6O_{21} \cdot 6\frac{1}{2}\ H_2O \cdot 1\frac{1}{2}\ NH_3$. An attempt was made to prepare a bismuth vanadate of Bi/V = 1/3. But on chemical analysis of the compound Bi/V was found to be 2/3 instead of 1/3. The same discrepancy was observed in the preparation of lead vanadate (an analogue of bismuth vanadate) by Bhattacharyya *et al.* [12]. Thus, the composition of the precipitated bismuth vanadate catalyst is not ultimately defined by the Bi/V ratio and the binary compound consequently formed.

Thermal analysis

The results of thermal analysis of bismuth vanadate (2/3) is shown in Table 2. DTA and TG curves of this vanadate are shown in Fig. 1. DTA curve shows that the vanadate undergoes endothermic (endo) changes at 110–260° (flat), 420–460° (flat), 665°, 928° and exothermic (exo) changes at 305° and 190°. In nitrogen atmosphere endo peaks are observed at 225°, 510°, 745° and exo peaks at 325° and 460°. The TG curve registers a total weight-loss of about 6.2% within the temperature range 110–290° which corresponds to the removal of six molecules of water

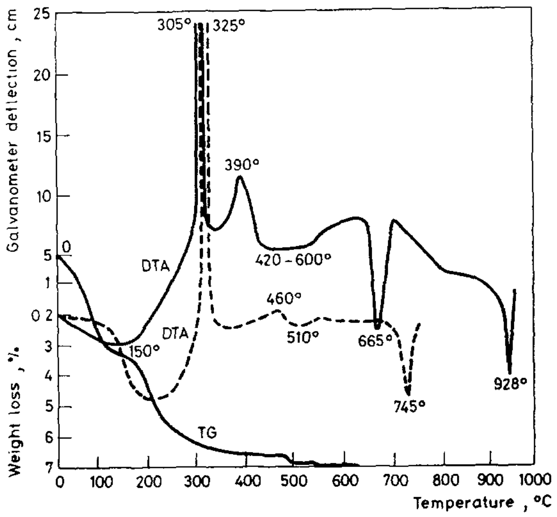


Fig. 1. DTA and TG of bismuth vanadate (2/3) in air and nitrogen atmospheres

Table 2

Results of thermal analysis (DTA and TG) bitmuth Bi-vanadates

Catalyst	Atmosphere	DTA Transitions				TG transitions, weight-loss, %
		Endothermic peak temp., °C	Range of temp., °C	Exothermic peak temp., °C	Range of temp., °C	
BV 2/3	Air	150	110–290	305	290–310	6.2, at 130–290°
		flat	420–600	390	320–400	1.2, at 290–310°
		665	640–690			
		928				
	N_2	225	210–295	325	300–340	
		510				
		745	710–760	460		
BV 3/1	Air	130	110–175	275	210–330	1.1, at 110–240°
		210				
		475	385–535	360		0.99, at 240–300°
	N_2	125	110–190	320	270–390	
		220				
		530	480–570	400	390–420	
BV 3/2	Air	185	110–205	330	290–350	2.5, at 110–205°
		290	215–320			
				365		1.8, at 215–320°
		flat				2.0, at 320–520°
		575	385–565			
		864				

and one molecule of ammonia from one molecule of the vanadate. Therefore, the flat peak at 110–260° is due to this reaction

$$Bi_4V_6O_{21}\cdot 6\tfrac{1}{2}\,H_2O\cdot 1\tfrac{1}{2}\,NH_3 \xrightarrow[-NH_3]{-H_2O} Bi_4V_6O_{21}\cdot \tfrac{1}{2}\,H_2O\cdot \tfrac{1}{2}\,NH_3$$

In nitrogen atmosphere all the exo peaks are retained with slight shift in transition temperature.

Infrared analysis

IR spectral data of all the samples are shown in Table 3. The significant bands observed at 950–720 cm^{-1} are assigned to the V–O stretching as observed in the case of polyvanadates [13]. The other bands at 3500–3200 cm^{-1} account for O–H stretching and those at 2350–2300 cm^{-1} are due to combination modes of the bending with vibration mode of water. The bands at 1625–1580 cm^{-1} are

Table 3

IR espectral data of Bi-vanadate samples

BV 2/3 110	3420 mb, 3200 mb, 2300 vw, 1620 mb, 1150 vw, 950 vw, 775 sb
BV 2/3 140	3420 mb, 3200 mb, 1625 msh, 1150 vw, 945 vw, 895 wsh, 780 sb
BV 2/3 260	3500 mb, 1625 msh, 960 vw, 770 mb.
BV 2/3 310	1005 sb, 830 vw
BV 2/3 400	1010 ssh, 830 mb
BV 2/3 600	1320 vw, 1150 vw, 1010 ssh, 800 vw
BV 2/3 720	1320 wsh, 1150 wsh, 1025 wsh, 1010 mb, 800 vw.
BV 3/1 110 & BV 3/1 210	3400 wb, 2340 msh, 1620 wb, 1320 vw, 1150 wb, 1010 vw, 720 mb.
BV 3/1 320	3540 wb, 3200 mb, 2320 wb, 1620 wb, 1155 wsh, 1130 wsh, 1060 wsh.
BV 3/1 370	2320 w, 1150 w.
BV 3/1 570 & BV 3/1 630	2340 wb, 1150 wsh, 720 mb.
BV 3/2 110	3400 vw, 2320 vw, 1150 vw, 720 mb.
BV 3/2 190	3400 vw, 2320 vw, 1150 vw, 830—650 sb.
BV 3/2 300 & BV 3/2 400	2320 vw, 1580 vw, 800—650 wb.
BV 3/2 530	890 wb, 780 wb.

Visually estimated intensities: v-very, s-strong, m-medium, w-weak, b-broad, sh-sharp

assigned to H—O—H bending and those at 1150—1130 cm^{-1} to V—O—H bending. The V—O stretching modes observed at two distinct regions 1000—900 cm^{-1} and 780—720 cm^{-1} indicate that there is one short VO bond at each vanaridium atom with the remaining VO bonds being appreciably longer and more variable. Thus, vanadium is $Bi_4V_6O_{21}$ may coordinate with either five or six oxygens, existing in the form of Zig-Zag chains of VO_6 octahedra, joined at centres to form corrugated sheets of layered structures. Table 3 indicates that this vanadate is completely dehydrated at a temperature less than or at 310°. Thus, the endo peaks prior to exo-ones are due to stepwise dehydration. The band at 1005 cm^{-1} in the spectrum of BV 2/3 310 may be due to the presence of excess ammonium metavanadate in the sample. However, the band at 1025 cm^{-1} of the sample BV 2/3 720 is due to V—O stretching of V_2O_5 or lower valent vanadium oxides [13]. It is evident from Table 3 that the common bands of all the samples undergo little shifting as a function of calcination temperature. It may be due to the removal of adsorbed oxygen at higher temperatures.

X-ray analysis

The results of X-ray analysis of various BV 2/3 samples are shown in Table 4. The XRD patterns of BV 2/3 110 and BV 2/3 140 samples were too vague to allow any identification. It appears that these samples are amorphous. The XRD patterns of BV 2/3 260 exhibit the lines with d = 3.177, 2.324, 1.918, 1.806 and 1.713 which indicate the presence of excess NH_4VO_3 (d = 3.17) or γ-Bi_2O_3 (d = 3.17)

Table 4

X-ray powder data Bi-vanadate (2/3) samples

BV 2/3 110 BV 2/3 140		BV 2/3 260		BV 2/3 310		BV 2/3 400		BV 2/3 600		BV 2/3 720	
*d*Å	*I*	*d*Å	*I*	*d*Å	*I*	*d*Å	*I*	*d*Å	*I*	*d*Å	*I*
		6.829		6.726	vvw						
6.525	vvw					5.837	vvw	5.837	vvw	5.837	vvw
6.525	vvw										
5.543	vvw										
5.333	vvw							5.333	vvw		
								5.032	vvw		
4.762	vvw	4.762	vvw	4.762	ms	4.762	s	4.762	ms		
						4.520	w			4.552	ms
				4.387	vw	4.387	m	4.387	ms	4.387	vs
		3.922	vvw			3.819	vw	4.102	vw	4.102	ms
				3.755	w					3.922	vw
3.755	vw					3.724	mw			3.755	vw
		3.177	ms	3.177	vs	3.412	mw	3.412	vw	3.465	vw
		3.024	vvw			3.177	vs	3.216	vw	3.216	vw
				2.923	ms	2.923	ms	3.083	vs	3.155	vs
		2.651	vw			2.746	w	2.923	ms	2.923	s
						2.651	ms	2.651	ms	2.651	ms
				2.547	ms	2.533	ms	2.547	ms	2.533	ms
				2.375	ms	2.464	vvw				
		2.339	vvw			2.312	s			2.238	ms
										2.238	ms
		2.324	mw					2.249	ms		
								2.175	vvw	2.175	s
2.282	vw					2.115	ms	2.115	ms	2.124	ms
		2.124	vvw	2.124	m	2.069	vw			2.050	m
				2.069	mw	1.973	mw	1.973	mw	1.933	m
		1.973	vw	1.973	ms	1.933	ms	1.933	m		
				1.933	s	1.918	ms	1.910	ms	1.910	ms
		1.918	mw			1.865	mw				
		1.858	vw			1.809	ms	1.809	ms	1.806	m
		1.806	mw	1.809	ms	1.769	mw	1.707	s	1.778	vvw
		1.713	m	1.713	s	1.707	s			1.707	s
				1.639	vw	1.677	vvw			1.639	m
				1.596	ms	1.639	mw	1.639	vw		
						1.571	m	1.571	ms	1.571	m
						1.542	ms	1.542	ms	1.561	ms

*d*Å — Interplanar spacing in angstrom unit.
I — visually estimated intensities: vs-very strong, s-strong, ms-medium strong m-medium, mw-medium weak, w-weak, vw-very weak, vvw-very very weak.

in the sample. This particular line with $d = 3.177$ may also be an indication for the interaction between NH_4VO_3 and $Bi(OH)_3$ at 260°. In the spectrum of BV 2/3 310 a number of characteristic lines, *viz.* with $d = 4.762$, 3.177, 2.923, 2.547, 2i.375, 1.973, 1.933, 1.713, 1.596 appear whereas the XRD patterns of BV 2/3 400 indicate the presence of almost all the lines except the shifting of the most characteristic line with $d = 3.177$ to $d = 3.083$. On the basis of d values of vanadium compounds available in ASTM file, the presence of the line with $d = 4.762$ is attributed to $H_8V_6O_{16}$ (ASTM card no. 11-368). XRD patterns of BV 2/3 600 are almost similar with those of BV 2/3 400. The only notable difference is the appearance of $d = 3.177$ line and missing of the line with $d = 3.08$. The presence of the line with $d = 4.387$ may be due to the formation of V_2O_5 ($d = 4.38$, ASTM card No. 9-148) by decomposition of adsorbed vanadate impurities. XRD patterns of BV 2/3 720 indicate the presence of $VO_{0\cdot 2}$, $VO_{0\cdot 9}$, V_2O_5, etc., along with the presence of a characteristic line with $d = 3.155$. The DTA curves may be interpreted in the light of the X-ray powder data. It is certain that the fresh BV 2/3 sample is amorphous or dis-ordered. However, at the temperature at which the exo peaks appear in the curve, the crystal structure becomes slightly ordered. It appears that on heating the reversion from dis-ordered 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 confirmed by the registration of negligible weight-loss in the TG curve in this temperature range as well as by the retention of exo peaks in nitrogen atmosphere. Smolyaninov *et al.* [8] already reported about the phase transition of $Bi_4(V_2O_7)_3$ at 200 – 280° and decomposition at 720°. Levy [7] also observed that $BiVO_x$, $Bi_4V_3O_x$, etc., undergo the formation of a new phase on being thermally treated. Roth *et al.* [10] observed the conversion of $BiVO_4$ (orthorhombic) to monoclinic $BiVO_4$ by subjecting it to prolonged heating at 500°.

Magnetic susceptibility measurements

All the BV 2/3 samples are diamagnetic. The various colour centres developed in course of thermal treatment, may, thus be due to reorganisation of the defects or displacement of oxygen anions which is typical in oxidation catalysts.

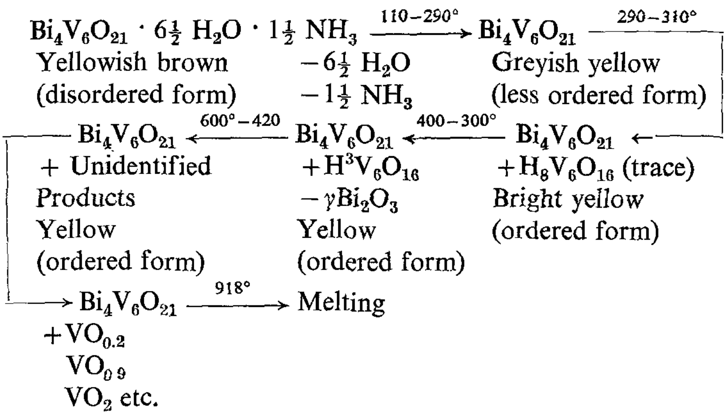
Surface area measurements

Surface areas (m^2/g) of some of the BV 2/3 samples are the following:

BV 2/3 260 – 23.5; BV 2/3 290 – 30.6; BV 2/3 310 – 29.5; BV 2/3 400 – 9.8; BV 2/3 500 – 36.8.

These values indicate that BV 2/3 is completely dehydrated at 290°. The maximum surface area corresponds to complete dehydration and the surface area gets reduced stepwise due to a series of phase changes. The higher surface area at 500° may be due to the presence of various oxides of vanadium at this temperature.

Summarizing all the findings, the thermal changes in BV 2/3 can be expressed as follows:



Bismuth vanadate (3/1) or BV 3/1

Preparation and chemical analysis

The composition of BV 3/1 has been established as $Bi_6V_2O_{14} \cdot 3\ H_2O$. An attempt was aimed at achieving a BV of Bi/V = 2/3 but on chemical analysis of the finished product Bi/V ratio is found to be 3/1 instead of 2/3. The same discrepancy was observed for BV 2/3 compound.

Thermal analysis

The results of DTA and TG of BV 3/1 are shown in Table 2. DTA and TG curves are shown in Fig. 2. In the DTA curve, a sharp endo peak appears at 130° followed by one endo dent at 210 , one broad exo peak at 275°, an endo hump at 350° and

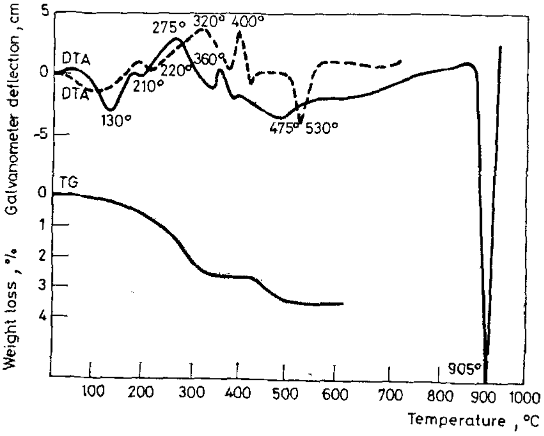


Fig. 2. DTA and TG of bismuth vanadate (3/1) in air and nitrogen atmospheres

an exo peak at 360°. There appears again one endo dent at 385 followed by a flat endo peak at 385 – 535 and a sharp endo change at 905°. In nitrogen atmosphere there occurs a considerable shift in all the transition temperatures. The first two endo peaks appear at 125 and 220° and other endo changes, at 420 and 530°.

The TG curve represents a gradual and slow weight-loss at 110 – 500 amounting to 3.33 % which corresponds to the removal of three molecules of water from one molecule of $Bi_6V_2O_{14} \cdot 3\,H_2O$. The weight-loss at different temperatures is calculated and the following sequences are obtained by stoichiometric considerations:

$$\begin{tikzcd}
Bi_6V_2O_{14} \cdot 3\,H_2O \arrow[r, "\text{up to } 240^\circ", "-H_2O"'] & Bi_6V_2O_{14} \cdot 2\,H_2O \arrow[d, "240-300^\circ", "-H_2O"'] \\
Bi_6V_2O_{14} & Bi_6V_2O_{14} \cdot H_2O \arrow[l, "300-500^\circ", "-H_2O"']
\end{tikzcd}$$

No weight-loss has been observed in the TG curve after 500 .

Infared analysis

IR spectra data of all the samples are shown in Table 3. The bands in the region 100 – 720 cm^{-1} are assigned to V – O stretching characteristic of polyvanadates.

Table 5

Results of X-ray analysis of Bi-vanadate (2/3) prepared by solid state reaction between Bi_2O_3 and V_2O_5

*d*Å	*I*	*d*Å	*I*	*d*Å	*I*	*d*Å	*I*
4.5706	wbr	1.5718	mbr	1.0249	w.br	0.8401	w
4.2643	vvw	1.5291	ms.br	0.9999	w.br	0.8401	w
3.0328	vvs	1.4576	vvw	0.9925	vvw	0.8155	mw
2.8657	w	1.4124	vvw	0.9843	vvw	0.8093	w
2.5657	vvw	1.3703	vvw	0.9689	vvw	0.8067	w
2.5136	vvw	1.3393	vw.br	0.9587	vvw	0.8052	w
2.2278	w.br	1.2978	vvw	0.9469	vvw	0.8005	w
2.1038	wm	1.2665	mw.br	0.9365	vvw	0.7990	w
1.9811	vw	1.2537	mw	0.9110	vvw.br	0.7914	w
1.9569	vvw	1.2397	mw	(?)	(?)	0.7887	w
1.9329	m	1.1814	w.br	0.8892	vvw.br	0.7862	w
1.9061	m	1.1667	w	0.8864	vw.br	0.7799	w
1.7966	w.br	1.1312	w.br	0.8770	vw.br	0.7768	w
1.7059	vs	1.1094	w.br	0.8713	mw		
1.6715	vvw	1.0598	w.br	0.8658	mw		
1.6412	vvw			0.8443	w		

*d*Å – Interplanar spacing in angstrom unit.

I – Visually estimated intensity, vvs = very very strong; vs = very strong; ms = medium strong m = medium; mw = medium weak; wm = weak medium; w = weak; vw = very weak vvw = very very weak; br = broad.

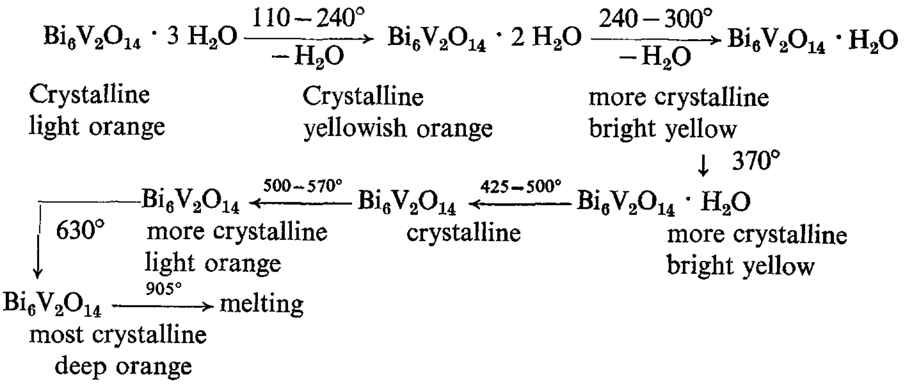
The assignment of other bands will be the same as done for BV 2/3 samples. IR data do not indicate any sort of decomposition at any stage of thermal treatment upto 630°.

X-ray analysis

The results of X-ray analysis of various BV 3/1 samples are shown in Table 6. Contrast to fresh BV 2/3 sample, BV 3/1 110 sample is well crystalline. A number of characteristic lines appear in the diffractogram of BV 3/1 110 sample as is evident from Table 6. The X-ray powder data indicate that dehydration and phase transitions in this vanadate is concurrent. Dehydration starts at 110° and ends at 500° whereas stepwise phase transitions start at 275° and end at 570°. The emergence of a strong line with $d = 3.177$ is accepted as an indication for the formation of a new phase. The same line was found to appear in the XRD patterns of BV 2/3 260 sample. This characteristic line is found to shift to $d = 3.083$ at 370° calcination temperature with enhanced intensity. This change may be due to the reorientation of BV 3/1 lattice. This reorientation continues upto 570° as is revealed by the shifting of $d = 3.083$ line to $d = 3.05$. The same line is retained in the XRD patterns of BV 3/1 630 sample. Thus, the exo peaks at 275° and 360° are due to phase changes.

Magnetic susceptibility measurements

All the BV 3/1 samples are diamagnetic. The various colour centres developed in course of thermal treatment may be due to reorganization or dislocation of defects, etc., which are typical in this class of catalysts. Summing up all the observations the thermal changes in BV 3/1 system can be expressed by the following scheme of reactions:



Bismuth Vanadate (3/2) or BV (3/2)

Preparation and chemical analysis

The composition of BV (3/2) is established as $Bi_6V_4O_{19} \cdot 6\,H_2O$.

Table 6

X-ray powder data of

BV 3/1 110		BV 3/1 210		BV 3/1 320	
*d*Å	*I*	*d*Å	*I*	*d*Å	*I*
6.928	vvw				
		6.726	vvw		
5.837	vvw	5.914	vvw	5.837	vw
4.870	ms	4.870	ms	4.870	ms
4.430	m	4.430	vw		
			4387		vw
				4.102	vw
				3.991	vw
3.663	vs	3.663	vs	3.887	vw
3.412	vw	3.412	vvw	3.634	vs
3.177	vvw	3.149	vw	3.177	s
3.042	vvw	3.042	vw		
2.923	ms			2.905	ms
		2.885	ms		
2.746	vs	2.776	s	2.730	s
				2.575	ms
2.575	s	2.575	ms	2.439	vw
				2.375	vw
2.271	ms	2.259	ms	2.271	vw
2.050	ms	2.175	vw	2.124	mw
1.918	ms	2.042	mw	2.078	mw
1.865	vs	1.918	ms	1.988	mw
1.823	ms	1.865	s	1.873	s
1.788	vw	1.809	ms	1.823	ms
1.672	vw	1.689	m	1.707	ms
1.622	m	1.612	m	1.617	m
1.510	ms				
1.466	ms				
1.418	vw				
1.358	m				

*d*Å — Interplanar spacing in angstrom unit.

Thermal analysis

The results of thermal analysis of BV 3/2 are shown in Table 2. DTA and TG curves are shown in Fig. 3. In the DTA curve, two sharp endo changes are observed at 185° and 290° followed by two sharp exo peaks of different magnitudes at 320°

Bi-vanadate (3/1) samples

BV 3/1 370		BV 3/1 570		BV 3/1 630	
*d*Å	*I*	*d*Å	*I*	*d*Å	*I*
5.837	vvw			5.837	vvw
		5.672	vvw		
4.870	ms	4.713	ms	4.713	s
4.565	vw				
4.387	vw			4.387	vw
3.887	vw			3.819	w
3.634	vs	3.755	vw		
				3.693	mw
				3.412	m
3.083	vs	3.050	vs	3.050	vs
2.923	ms			2.923	s
2.746	s	2.779	ms		
2.575	ms	2.575	ms	2.720	ms
		2.533	ms	2.651	ms
2.271	ms	2.238	ms	2.533	ms
2.124	vvw	2.115	ms		
2.060	w	1.973	ms	2.400	mw
1.910	m	1.949	s	2.352	w
1.865	s	1.873	m	2.249	ms
1.809	mw	1.802	ms	2.124	ms
1.707	m	1.707	s	1.957	ms
		1.666	mw	1.933	ms
		1.626	mw	1.910	ms
		1.571	mw	1.809	ms
		1.546	ms	1.707	s
				1.649	ms
				1.622	s
				1.592	s
				1.409	m

I — visually estimated intensities: vs-very strong, s-strong, ms-medium strong, mw-medium weak, w-weak, vw-very weak, m-medium, vvw-very very weak.

and 365°. A flat endo peak appears at 385–565° followed by an endodent at 575°. The last endo peak is, however, noticed at 864°.

The TG curve of BV 3/2 records a total weight-loss amounting to 6.3% at 110–520° which corresponds to the removal of six molecules of water from one molecule of $Bi_6V_4O_{19} \cdot 6\,H_2O$. Two weak and less defined plateaux appear in the

TG curve at 110–320° suggesting the possibility of formation of two intermediate stages in the course of dehydration. But after 320°, there is a continuous weight-loss upto 460° followed by slow weight-loss till 625°. From the projection of the peaks of the DTA curve on the TG curve, the following sequences are suggested by stoichiometric considerations for the dehydration process:

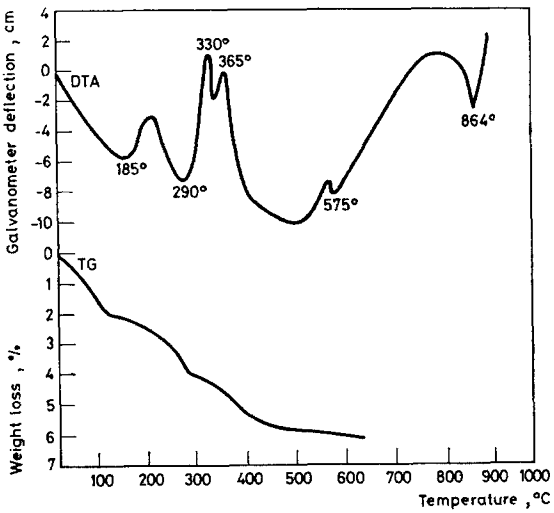


Fig. 3. DTA and TG of bismuth vanadate (3/2) in air

$$\begin{tikzcd}
Bi_6V_4O_{19}\cdot 6.H_2O \arrow[r, "110-205^\circ", "-2\,H_2O"'] & Bi_6V_4O_{19}\cdot 4.H_2O \arrow[d, "-2\,H_2O"', "215-320^\circ"] \\
Bi_6V_4O_{19} & Bi_6V_4O_{19}\cdot 2\,H_2O \arrow[l, "320-520^\circ"', "-2\,H_2O"]
\end{tikzcd}$$

Infrared analysis

IR spectral data of all the BV 3/2 samples are shown in Table 3. The bands in the region 890–650 cm^{-1} are assigned to the V–O stretching characteristic of polyvanadates. The other bands may be assigned as done in the earlier cases. The strong band of BV 3/2 190 sample at 830–650 cm^{-1} appears to be coupled with frequency, characteristic of water. This band becomes very weak when the compound is heated at 400°. At 530°, BV 3/2 is completely dehydrated as is revealed by the absence of the bands, characteristic of water in the spectrum of BV 3/2 530 sample. Two bands at 890 and 780 cm^{-1} at this stage are indicative of V–O stretching of the polyvanadates.

X-ray analysis

X-ray powder data of BV 3/2 110 sample indicate that crystal structure of BV 3/2 is completely dis-ordered, i.e. amorphous. This amorphous nature is retained upto 290°. At 530°, the structure of BV 3/2 is almost ordered as is revealed by the presence of strong lines with $d = 3.1051$ (characteristic), 2.7756, 2.5815 and 1.9750 etc. Thus, the exochanges at 330° and 365° are due to disorder–order transitions.

Magnetic susceptibility measurements

All the BV 3/2 samples are diamagnetic. No colour change of this compound was visible althrough the investigation. Summarizing all the data, the thermal changes in BV 3/2 can be expressed as follows:

$$\begin{tikzcd}
\underset{\text{(dis-ordered form)}}{Bi_6V_4O_{19}\cdot 6\,H_2O} \arrow[r, "110-205^\circ", "-2\,H_2O"'] & Bi_6V_4O_{19}\cdot 4\,H_2O \arrow[r, dash, "215-320^\circ", "-2\,H_2O"'] & {} \arrow[d] \\
\text{Melting} & \underset{\text{(almost ordered form)}}{Bi_6V_4O_{19}} \arrow[l, "864^\circ"'] & Bi_6V_4O_{19}\cdot 2\,H_2O \arrow[l, "320-520^\circ"', "-2\,H_2O"]
\end{tikzcd}$$

Solid state reaction between Bi_2O_3 and V_2O_5

Bi_2O_3 and V_2O_4 were mixed in the ratio 2 : 3, fused at high temperature and used for comparison. The compound prepared by this method, has been found to have the composition $Bi_4V_6O_{21}$ or $2\,Bi_2O_3 \cdot 3\,V_2O_5$. The results of X-ray analysis of this compound as shown in Table 5 indicate that its crystal structure is essentially the same as is observed in the case of BV 2/3 400. Thus, it is certain that solid state reaction between Bi_2O_3 and V_2O_5 components takes place in our BV samples and the strong line with $d = 3.03 - 3.17$ may be an indication for the same.

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RÉSUMÉ — Les propriétés physico-chimiques des catalyseurs au vanadate de bismuth, de diverses compositions, par ex. $Bi_4V_6O_{21} \cdot 6\frac{1}{2}H_2O \cdot 1\frac{1}{2}NH_3$, $Bi_6V_2O_{14} \cdot 3\,H_2O$, $Bi_6V_4O_{19} \cdot 6\,H_2O$, ont été étudiées par analyse chimique, analyse thermique différentielle, thermogravimétrie, spectroscopie infrarouge, diffraction des rayons X, mesures de surfaces spécifiques et de susceptibilité magnétique.

Dans tous les cas, les phénomènes endothermiques qui précèdent ceux de nature exothermique sont dus à la déshydratation par étapes; les phénomènes endothermiques qui suivent ceux de nature exothermique sont dus aux impuretés adsorbées, au frittage, à la fusion, etc... Cependant, le dernier pic endothermique est toujours dû à la fusion. Les changements exothermiques sont attribués à des transitions de phases par étapes. La déformation V—O dans tous les composés est caractéristique des polyvanadates. Deux types de liaisons vanadium-oxygène, par ex. $V = O$ et $V—O—V$ ont été caractérisés par analyse infrarouge. Le premier et le troisième vanadate, fraîchement préparés, sont amorphes alors que le second est cristallisé. Les phénomènes exothermiques (probablement dus à des transitions désordre-ordre) sont sans doute en rapport avec le déplacement des anions oxygène. Les vanadates précipités — si on les chauffe jusqu'à une température élevée — sont similaires aux produits correspondants, obtenus par réaction à l'état solide entre Bi_2O_3 et V_2O_5. Les vanadates fraîchement préparés ainsi que ceux qui ont subi un traitement thermique, sont diamagnétiques. Ces systèmes montrent une surface spécifique maximalé à la température correspondant à la déshydratation complète. La composition des vanadates précipités n'est pas finalement définie par le rapport Bi/V et le composé binaire formé par la suite.

ZUSAMMENFASSUNG — Die physikalisch-chemischen Eigenschaften von Bismuthvanadat-Katalysatoren verschiedener Zusammensetzung, z. B. $Bi_4V_6O_{21} \cdot 6\frac{1}{2}\,H_2O \cdot 1\frac{1}{2}\,NH_3$; $Bi_6V_2O_{14} \cdot 3\,H_2O$; $Bi_6V_4O_{19} \cdot 6\,H_2O$ wurden durch chemische Analyse, Differentialthermoanalyse, Thermogravimetrie, Infrarot, Röntgendiffraktion, Oberflächenmessung und magnetische Susceptibilitätsmessung untersucht. In jedem Fall werden die den Exo-Änderungen vorangehenden Endo-Änderungen durch stufenweise Dehydratisierung verursacht und diejenigen, welche den Exo-Änderungen folgen, durch Zersetzung adsorbierter Verunreinigungen, Sinterung und Schmelzen. Der letzte Endopeak ist jedoch in jedem Falle dem Schmelzen zuzuschreiben. Die Exo-Änderungen werden stufenweisen Phasenübergängen zugeschrieben. In allen Verbindungen ist die V—O Dehnung für die Polyvanadate charakteristisch. Zwei Typen von Vanadium-Sauerstoff Bindungen, z. B. $V = O$ und $V—O—V$ wurden durch IR-Analyse charakterisiert. Die frisch synthetisierten ersten und dritten Vanadate sind amorph, während das zweite kristallin ist. Die (vermutlich durch Unordnung—Ordnungs Übergänge verursachten) Exo-Änderungen sind wahrscheinlich mit der Bewegung der Sauerstoff-Anionen verbunden. Die gefällten Vanadate sind — wenn sie auf hohe Temperaturen erhitzt werden — ihren entsprechenden Festphasen-Reaktionsprodukten Bi_2O_3 und V_2O_5 ähnlich. Die ursprünglichen wie die behandelten Vanadate sind diamagnetisch. Diese Systeme weisen die maximale Oberfläche bei der ihrer vollständigen Dehydratisierung entsprechenden Temperature auf. Die Zusammensetzung der gefällten Vanadate wird letzten Endes nicht durch ihr Bi-V-Verhältnis und die in der Folge entstandene Binärverbindung bestimmt.

Резюме — Физико-химические свойства висмут-ванадатных катализаторов различного состава, например, $Bi_4V_6O_{21} \cdot 6.5\ H_2O \cdot 1.5\ NH_3$; $Bi_6V_2O_{14} \cdot 3H_2O$; $Bi_6V_4O_{19} \cdot 6H_2O$ были изучены химическим анализом, дифференциальным термическим анализом, термогравиметрией, ИК спектроскопией, рентгено-диффракционным методом, определением поверхностной площади и методом магнитной восприимчивости. Во всех случаях, эндоизменения до первого из экзоизменений, обусловлены ступенчатой дегидратацией, а последующие экзоизменения обусловлены разложением адсорбированных примесей, спеканием, плавлением и т. д. Однако последний эндопик всегда обусловлен плавлением. Экзоизменения отнесены к ступенчатым фазовым переходам. Во всех соединениях V—O валентные колебания характеризуют поливанадаты. С помощью ИК спектроскопии охарактеризованы два типа связей ванадий-кислород: V = O и V—O—V. Свежеприготовленные первый и третий ванадаты являются аморфными, в то время как второй — кристаллический. Предположено, что экзоизменения (по-видимому, обусловлены переходами беспорядок-порядок) должны быть связаны со смещением анионов кислорода. Осажденные ванадаты подобны соответствующим реакционным продуктам, полученным в результате твердотельной реакции Bi_2O_3 и V_2O_5 при нагреве их при повышенной температуре. Как свежеприготовленные, так и обработанные ванадаты являются диамагнитными. Эти системы показывают максимум поверхностной площади при температуре, соответствующей их полной дегидратации. Состав осажденных ванадатов в конечном счете не определяется соотношением Bi/V, а, следовательно, образуется бинарное соединение.