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Preparation and Activity of Bismuth Tungstates in Oxidation and Ammoxidation of Olefins*

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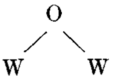
Investigations have been carried out on the catalytic behavior of Bi tungstates at the different ratios Bi/W: 2/3, 1/1, 1.8/1, 2/1, 6/1 in the oxidation and ammoxidation of propylene and 1-butene.

Bi_2WO_6 is the only active and selective compound. WO_3 is active but the main products of oxidation of both 1-butene and propylene are CO and CO_2. At low temperatures WO_3 shows a high isomerizing power towards 1-butene while Bi_2WO_6 is inactive.

Ammonia present in the reagent mixture modifies the catalytic behavior of WO_3, keeping the distribution of products of ammoxidation of olefines nearer to the distribution given by Bi_2WO_6.

The surface acidic sites and the formation of CO and CO_2 were attributed to the presence of



$W \overset{O}{\diagup\diagdown} W$

bonds of covalent type. These types of bonds are not present in Bi_2WO_6 which has a rather polar structure.

INTRODUCTION

Both bismuth molybdates and tungstates are well known catalysts for ammoxidation of propylene (*1*, *2*) and for the oxidation of butene (*1*, *2*). Bi tungstates are less active and selective than Bi molybdates. The maximum of activity for Bi tungstates as for Bi molybdates was observed for Bi/W and Bi/Mo ratios in the range from 2/3 to 2/1 (*1*, *2*).

In this range, different from Bi molybdates (*3*, *4*), very little difference in activity of Bi tungstates was observed for both the ammoxidation of propylene (*5*) and the oxidation of butenes (*6*). In contrast to Bi molybdates (*3*, *4*), in the range from 2/3 to 2/1, only two compounds, $Bi_2(WO_4)_3$ and Bi_2WO_6 (*7*–*9*) exist for certain. As can be easily deduced from the data reported by Gal'perin, Erman and Kolchin (*7*) and by Margolis (*2*), the existence of $Bi_2W_2O_9$ is doubtful.

In this work we have aimed at preparing well-characterized Bi tungstates so as to clarify (a) whether their activity in oxidation is really structure independent, and (b) the nature of Bi tungstates that can exist at the normal temperature of activation of the catalysts.

EXPERIMENTAL METHODS

Preparation of Catalysts

Bi tungstates with Bi/W ratio 1/1 were prepared by adding a solution of $Bi(NO_3)_3 \cdot 5H_2O$ at pH 2.2 and 80°C (10 moles in 1000 ml of deionized water) to a solution of $Na_2WO_4 \cdot 2H_2O$, at the same pH and temperature (10 mmoles in 1600 ml of deionized water). After precipitation the solution was immediately filtered and analyses were carried out for the presence of Bi^{III} and W^{VI} in the filtrates. Only traces of Bi^{III} were observed. Several preparations were carried out with the above precipitation conditions, increasing the amount of W^{VI} in the initial solutions so as to reach a Bi/W

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ratio equal to 2/3. From the analysis of the filtrates we calculated the composition of the precipitates and always obtained a result of a Bi/W ratio equal to 1/1.

Using the same precipitation with a ratio Bi/W equal 2/1 in the starting solution we obtained a result of ratio Bi/W equal 1.8/1 in the precipitate. Bi tungstates with Bi/W ratio exactly equal to 2/1 were prepared precipitating them from a solution with a high Bi/W ratio, i.e., by adding a solution of $Na_2WO_4 \cdot 2H_2O$ (5 mmoles in 800 ml of deionized water) at pH 2.2 and temperature 80°C to a solution of $Bi(NO_3)_3 \cdot 5H_2O$ (20 mmoles in 1000 ml of deionized water) at the same pH and temperature. Analysis of the filtrate showed the Bi/W ratio in the precipitate to be exactly 2. As Bi was present in great excess the filtration had to be carred out as soon as possible because Bi hydroxide gradually precipitates in the solution and it was therefore necessary to separate the precipitate of Bi tungstate 2/1 before this could take place.

Bi tungstate 6/1 was prepared by solid state reaction between Bi_2WO_6 and Bi_2O_3 at 600°C for 2 hr.

A tentative preparation of Bi tungstates with a Bi/W ratio 2/3 was carried out by analogy with Bi molybdates 2/3 (*10*) changing the precipitation conditions to 20°C and pH 1.5 and with an initial Bi/W ratio in the solution equal to 2/3. Analysis of the filtrates showed that the resulting Bi/W ratio in the precipitate was always equal to 1/1.

Tentative preparation of Bi tungstates with different Bi/W ratios were realized by solid state reactions at different temperatures both between pure oxides and Bi tungstates 1/1 or pure oxides and Bi tungstates 2/1.

WO_3 was prepared by pouring a solution of ammonium paratungstate (5 g in 150 ml of water) into concentrated nitric acid (300 ml) and boiling for 30 min before filtration.

Infrared Analyses

Infrared spectra were recorded using KBr discs and a grating spectrometer (Perkin-Elmer 457).

X-Ray Powder Data

X-Ray diffraction patterns were recorded with a Geiger-counter Philips spectrogoniometer with Cu $K\alpha$ radiation.

Electronic Spectra

Electronic spectra were recorded with a Cary 15 spectrophotometer with a diffuse reflectance attachment.

Thermal Balance

Temperatures of onset of bulk reduction were measured with a thermal balance Adamel TH 59-2 with a 50 liters/hr flow of He and H_2 mixture (20% H_2 by vol).

Calcination

Catalysts were dried at 120°C for 2 hr and then calcined at the various temperatures of 350, 400, 500, and 600°C, always for 2 hr. Catalysts prepared by solid state reaction were also calcined but at temperatures higher than 600°C.

Measurements of Activity

The reactor used was a flow microreactor made of quartz. The amount of catalyst used for all tests was 1.5 g, each grain of catalyst having dimensions of about 1 mm.

The concentrations of the reactants for oxidation and ammoxidation were, respectively, 2% butene by volume and 2% butene plus 2% NH_3; for oxidation and ammoxidation of propylene they were, respectively, 3% propylene and 3% propylene plus 3% NH_3, the rest being air of chromatographic grade.

For the analysis of reaction products two gas chromatographs were used: on the first (Fractovap Carlo Erba, model C), a 6.5 m column with dimethysulfolane on Chromosorb P AW was set up with which air, CO_2, 1-butene, *trans*- and *cis*-2-butenes and butadiene were recorded and a 0.70 m column of molecular sieves with which O_2, N_2, CO were recorded.

On the second gas chromatograph (Hewlett-Packard, model 5750), a 1.90 m column of dinonyl-phthalate on Chromosorb G AW DMCS was set up with which the other oxidation products were recorded (e.g., acrolein and acrylonitrile).

Results

Characterization of Catalysts

In Figs. 1 and 2 the ir and electronic spectra of the catalysts are respectively reported. X-Ray data are given in Table 1, and in Table 2 the temperature of onset of bulk reduction of the catalysts is reported.

Bi Tungstate 2/1

The X-ray pattern of this catalyst is the same as reported for Bi_2WO_6 by Gal'perin, Erman and Kolchin (*7*) with characteristic *d* values at 3.147, 2.72, 1.92, 1.62 Å. The ir spectrum is practically the same as reported for Bi_2MoO_4 (*10*). No modification in the ir, X-ray and electronic spectra were observed during calcination from 400 to 600°C.

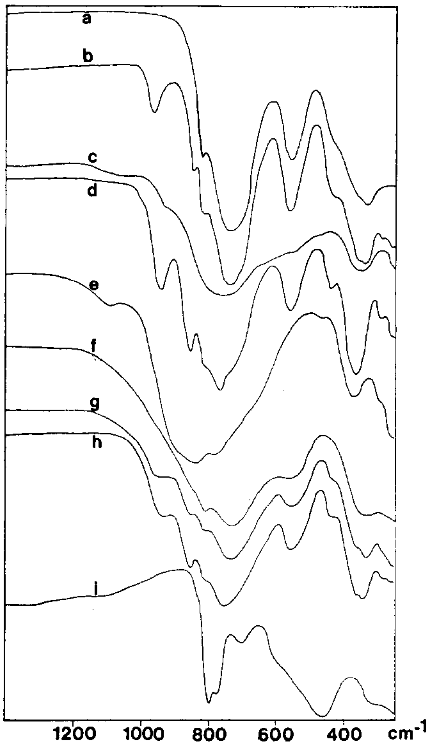

FIG. 1. Infrared spectra of the catalysts: (a) Bi-W 2/1 calcined at 500°C for 2 hr; (b) Bi-W 1.8/1 calcined at 500°C for 2 hr and at 600°C for 2 hr; (c) Bi-W 1/1 calcined at 500°C for 2 hr; (d) Bi-W 1/1 calcined at 500°C for 2 hr and 600°C for 2 hr; (e) WO_3 calcined at 500°C for 2 hr; (f) Bi-W prepared by solid state reaction by calcination at 500°C for 11 hr; (g) Bi-W prepared as in (f), with a further calcination at 600°C for 2 hr; (h) Bi-W prepared as in (f), with a further calcination at 700°C for 2 hr; (i) Bi-W calcined at 500°C for 2 hr and at 600°C for 2 hr.

Bi Tungstate 1.8/1

The X-ray pattern of this catalyst calcined at 600°C is the same as that of Bi_2WO_6. The ir spectrum presents all the bands of Bi_2WO_3 (at 815, 735, 555 and 335 cm^{-1}) with some new bands (at 955, 850 and 435 cm^{-1}). We have attributed these bands to traces of $Bi_2(WO_4)_3$ (Fig. 1h). The electronic spectrum of this catalyst is practically the same as that of Bi_2WO_6.

Bi Tungstate 1/1

The X-ray patterns of the samples calcined at 400 and 500°C showed that the samples were amorphous having only a broad low peak with its maximum at *d* = 3.15 Å. Samples calcined at 600°C presented a characteristic spectrum with *d* = 3.209; 2.973; 2.702; 1.914; 1.646 Å as reported for $Bi_2(WO_4)_3$ by Gal'perin, Erman and Kolchin (*7*). No new bands of other compounds were observed. However, another compound with a high Bi content must be present. In the case of $Bi_2Mo_2O_9$ it has been suggested (*11*) that it decomposes at 400°C to $Bi_2(MoO_4)_3$ and Bi_2MoO_6.

The mechanism of the decomposition of Bi tungstate 1/1 does not give rise principally to Bi_2WO_6, since if present it should be in a high percentage (37% by wt) and therefore its characteristic X-ray pattern should be observed. However, we cannot exclude the presence of traces. Also from the ir spectrum there is no evidence of the formation of Bi_2WO_6. In fact, bands are present at 940, 855, 760, 555, 435 and 360 cm^{-1}. These bands are different from those of Bi_2WO_6 and are characteristic of $Bi_2(WO_4)_3$ (Fig. 1h). There is also no evidence of the presence of Bi_2O_3 because this has a strong absorption in the electronic spectrum (see Fig. 2) from 415 to 320 nm and at 265 nm.

For Bi tungstate 1/1 calcined at 600°C we propose the presence, besides Bi tungstate 2/3, of a compound like Bi_6WO_{12} and

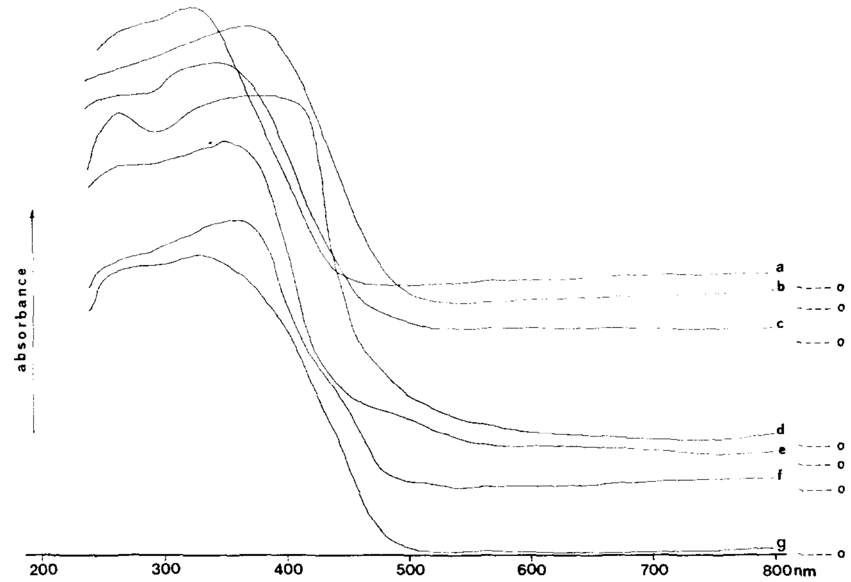

FIG. 2. Electronic spectra of the catalysts: (a) Bi–W 2/1 calcined at 500°C for 2 hr; (b) Bi–W 1/1 calcined at 500°C for 2 hr; (c) Bi–W 1/1 calcined at 500°C for 2 hr and at 600°C for 2 hr; (d) Bi_2O_3 calcined at 500°C for 2 hr; (e) Bi–W 6/1 calcined at 500°C for 2 hr and at 600°C for 2 hr; (f) Bi–W 2/3 prepared by solid state reaction by calcination at 500°C for 11 hr and 700°C for 2 hr; (g) WO_3 calcined at 500°C for 2 hr.

TABLE 1

X-RAY DATA OF Bi TUNGSTATES CALCINED AT DIFFERENT TEMPERATURES (*d* VALUES AND RELATIVE INTENSITIES)

WO_3 500°C		Bi/W 1/1; 600°C		Bi/W 2/1; 400°C		Bi/W 2/1; 600°C		Bi/W 6/1; 600°C		Bi/W 2/3; 500°C		Bi/W 2/3; 700°C	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
3.817	94	3.929	5	3.147	100	3.952	4	3.243	100	3.841	24	11.76	9
3.739	94	3.767	33	2.726	51	3.147	100	2.894	3	3.739	14	3.934	11
3.632	100	3.420	9	2.488	4	2.719	57	2.801	35	3.618	16	3.842	13
3.326	22	3.209	73	1.925	39	2.491	4	2.755	4	3.333	8	3.784	36
3.079	29	2.973	100	1.643	39	1.925	49	1.996	4	3.216	14	3.639	13
2.678	41	2.702	96	1.576	11	1.617	61	1.981	30	3.142	100	3.446	42
2.610	54	1.994	8			1.575	12	1.687	21	2.713	39	3.207	86
2.511	10	1.914	64					1.665	3	2.622	10	3.147	37
2.156	18	1.890	20					1.619	5	2.162	6	2.973	100
2.014	6	1.646	86							1.925	30	2.706	78
1.917	9	1.606	10							1.824	5	2.610	7
1.875	10	1.549	23							1.687	5	2.003	23
1.821	26									1.640	41	1.925	13
1.706	11									1.572	6	1.915	41
1.688	10											1.894	22
1.669	13											1.648	73
1.639	25											1.613	21
1.532	9											1.574	6
												1.552	26

TABLE 2
Temperature of Onset of Bulk Reduction of Bi Tungstates

Catalyst		Calcination temp (°C)	Temp of onset of bulk reduction (°C)
Bi/W	2/1	500	490
	2/1	600	490
	1.8/1	600	490
	1/1	500	540
	1/1	600	505
	6/1	600	435
WO_3		500	490

eventual traces of Bi_2WO_6. This compound should be present in low percentage and would therefore be undetected by X-ray techniques. This compound, moreover, has an electronic spectrum similar to Bi tungstate 1/1 calcined at 600°C (see Fig. 2).

As far as Bi tungstate 1/1 calcined at 500°C is concerned, we conclude from the ir and electronic spectra, and the high temperature of bulk reduction (Table 2), that it is a compound different from $Bi_2(WO_4)_3$ and Bi_2WO_6. This compound may be analogous to $Bi_2Mo_2O_9$ (*10*). However, we shall characterize it as Bi_2O_3–$2WO_3$.

WO_3

In Figs. 1 and 2 the electronic and ir spectra of WO_3 are reported. In Table 1 the X-ray pattern of WO_3 dried at 130°C for 3 hr and calcined at 500°C for 2 hr is reported.

Bi Tungstate 6/1

From the ir and X-ray data (see Fig. 1 and Table 1) we propose that solid state reaction at 600°C as reported in the Experimental section leads to a well-characterized compound.

Bi Tungstate 2/3

X-Ray patterns and ir spectra show that the product of solid state reaction between Bi_2O_3 and WO_3 with a Bi/W ratio of 2/3 is, after calcination at 500°C for 11 hr, a mixture of Bi_2WO_6 and WO_3, (Fig. 1 and Table 1). After calcination at 600°C for 2 hr some $Bi_2(WO_4)_3$ was formed as can be deduced from the ir spectrum (Fig. 1, bands at 940 and 855 cm^{-1}).

Calcining the powder at 700°C for 2 hr yields a mixture in which the greatest part is $Bi_2(WO_4)_3$ (peaks at $d = 3.207$; 2.973; 2.706; 1.648 and bands at 940, 855, 755, 555, 435 and 340 cm^{-1}), although some, Bi_2WO_6 (peaks at $d = 3.147$; 1.925; 1.613; 1.574) and some WO_3 (peaks at $d = 3.632$; 2.610) are present as impurities.

Measurement of Activity

In Figs. 3, 4 and 5 we report the conversion of 1-butene and the amount of products formed against the temperature of reaction for WO_3, Bi tungstate 2/1 (calcined at 600°C) and Bi tungstate 1/1.

Tables 3 and 4 show, respectively, the results of the oxidation runs of 1-butene and propylene both in the presence and absence of NH_3 for comparison at two different temperatures.

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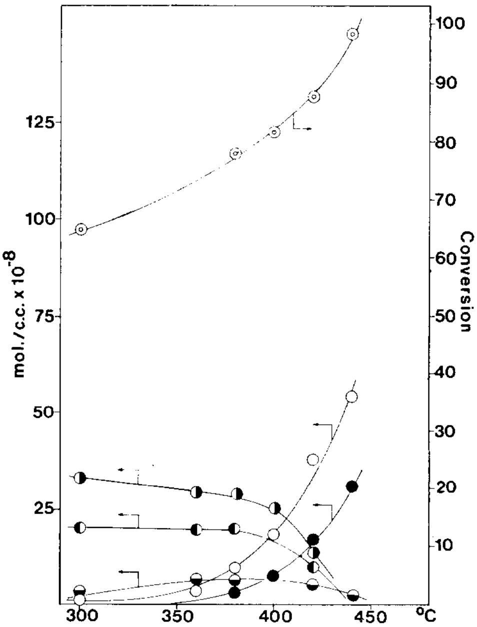


Fig. 3. Conversion of 1-butene with WO_3 calcined at 500°C for 2 hr. Experimental conditions: 2% 1-butene in air; weight of catalyst, 1.5 g; gas flow, 70 ml/min. (◎) 1-Butene conversion; (○) CO_2/4; (●) CO/4; (◑) *trans*-2-butene; (◐) *cis*-2-butene; (◒) butadiene.

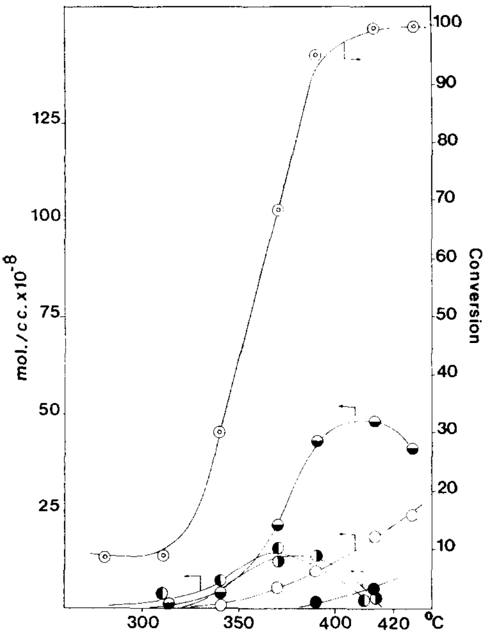


FIG. 4. Conversion of 1-butene with Bi tungstate 2/1 calcined at 500°C for 2 hr and at 600°C for 2 hr. Experimental conditions: 2% 1-butene in air; weight of catalyst, 1.5 g; gas flow, 70 ml/min. (◎) 1-Butene conversion; (○) $CO_2/4$; (●) CO/4; (◑) *trans*-2-butene; (◐) *cis*-2-butene; (◒) butadiene.

1-butene other products such as acetaldehyde, acetic acid and formaldehyde were obtained but were not identified. In the ammoxidation of propylene HCN and CH_3CN were observed but were not recorded quantitatively.

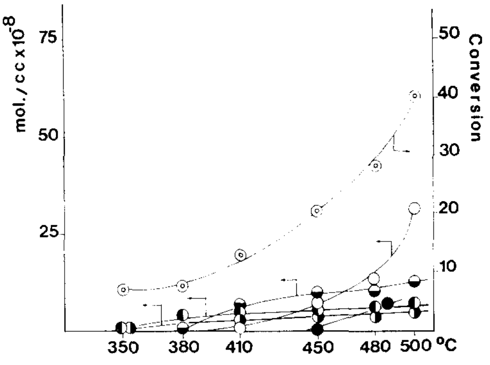


FIG. 5. Conversion of 1-butene with Bi tungstate 1/1 calcined at 500°C for 2 hr and 600°C for 2 hr. Experimental conditions: 2% 1-butene in air; weight of catalyst, 1.5 g; gas flow, 70 ml/min. (◎) 1-Butene conversion; (○) $CO_2/4$; (●) CO/4; (◑) *trans*-2-butene; (◐) *cis*-2-butene; (◒) butadiene.

Bi_6WO_{12} and Bi tungstate 1/1 calcined at 500°C were inactive in the range of temperature from 300 to 500°C.

The catalytic behavior of Bi tungstate 1.8/1 was the same as that of Bi tungstate 2/1.

DISCUSSION

The Relationship Between Structure and Catalytic Activity

Our results show that only WO_3 and Bi_2WO_6 are active as oxidation catalysts. The activity of Bi tungstate 1.8/1 calcined at 600°C can easily be attributed to Bi_2WO_6, which is the main compound present in it.

TABLE 3

OXIDATION AND AMMOXIDATION DATA FOR 1-BUTENE

Catalyst	Temp of reaction (°C)	Type of reaction	% Conversion[a]	$CO_2/4$ (moles/ml × 10^{-8})	CO/4 (moles/ml × 10^{-8})	*trans*-2-Butene (moles/ml × 10^{-8})	*cis*-2-Butene (moles/ml × 10^{-8})	Butadiene (moles/ml × 10^{-8})
Bi/W 2/1	390	Oxid.	68	5.1	1.91	13.3	14.1	21.5
		Amm.	12	0.88	—	0.302	0.507	2.24
WO_3	340	Oxid.	70	0.90	—	30	19.6	1.1
		Amm.	9	0.45	—	—	—	—
	440	Oxid.	97	54.0	31	0.65	0.64	2.2
		Amm.	82	7.20	1.09	22.9	15.65	5.55

[a] All runs had a constant gas flow of 70 ml/min and 2% 1-butene in air for the oxidation, and in the case of ammoxidation 2% 1-butene and 2% NH_3.

TABLE 4

OXIDATION AND AMMOXIDATION DATA FOR PROPYLENE

Catalyst	Temp of reaction (°C)	Type of reaction	% Conversion[a]	$CO_2/3$ (moles/ml × 10^{-8})	CO/3 (moles/ml × 10^{-8})	Acrolein (moles/ml × 10^{-8})	Acrylonitrile (moles/ml × 10^{-8})
Bi/W 2/1	430	Oxid.	63.8	26.3	5.55	130	—
		Amm.	56.4	4.93	—	—	140
WO_3	435	Oxid.	35	47.7	35.4	5	—
		Amm.	13	2.84	—	—	12

[a] All runs had a constant gas flow of 70 ml/min and 3% propylene in air for the oxidation, and in the case of ammoxidation 3% propylene and 3% NH_3.

The very low activity of Bi tungstate 1/1 calcined at 600°C can be attributed to $Bi_2(WO_4)_3$, but we cannot exclude that it is due to the presence of traces of Bi_2WO_6.

Our results do not agree with those of other authors who have not found strong differences in activity in Bi tungstates with Bi/W ratios from 2/3 to 2/1 (*2*, *3*). However, our results do agree with Batist *et al.* (*4*) in that Bi/Mo 2/1 is the most active compound among Bi molybdates.

The main difference between WO_3 and Bi_2WO_6 is not in the activity but in the selectivity in oxidation products and in the different acidity. WO_3 at low temperatures (where Bi_2WO_6 is inactive) presents a strong isomerizing power for 1-butene to 2-butenes. At high temperature, the products of oxidation of 1-butene and of propylene with WO_3 are essentially CO and CO_2 and traces of oxidized compounds of low molecular weight. In the case of Bi_2WO_6 the main product of oxidation of 1-butene is butadiene, and of propylene it is acrolein.

The presence of NH_3 in the gas phase in oxidation of 1-butene and propylene modifies the catalytic behavior of WO_3 in the same direction as the presence of Bi in the catalysts. The activity of WO_3 can be observed in Table 3 showing that the presence of NH_3 strongly reduces the activity and the isomerizing power, in particular of WO_3 at low temperature. At high temperature the presence of NH_3 strongly decreases the formation of CO and CO_2 and increases the formation of butadiene. In the case of ammoxidation of propylene (see Table 4) there is a strong decrease of CO and CO_2 and a high amount of acrylonitrile is formed.

As far as Bi_2WO_6 is concerned, the influence of NH_3 in oxidation of propylene is less marked than for WO_3. The amount of acrylonitrile formed is only slightly greater than the amount of acrolein formed in oxidation. However, much lower amounts of CO and CO_2 were observed in ammonoxidation. In the case of oxidation of 1-butene, NH_3 gives rise to a strong reduction in activity of Bi_2WO_6.

In order to discuss the mechanism by which the presence of Bi in the catalyst and NH_3 in gas phase decrease the amount of CO, CO_2 formed in oxidation of both 1-butene and propylene, and the acidity at low temperature shown by WO_3, it is necessary to analyze the structure of WO_3 and Bi_2WO_6.

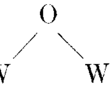
WO_3 presents a distorted octahedral coordination of W (*13*). In Table 5 the lengths of the W–O bonds are reported. The bond distances with $d = 1.72$, 1.79 Å present a double-bond character. The bond distances

TABLE 5

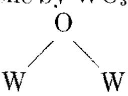
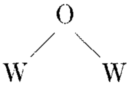
W–O BOND LENGTHS IN WO_3 (*13*) AND Bi_2WO_6 (*14*)

WO_3 (Å)	Bi_2WO_6 (Å)
1.89	1.69
1.91	1.69
1.72	1.82
2.16	1.82
2.13	2.30
1.79	2.30

with d = 1.91, 2.13, 2.16 Å are attributed to  $\mathrm{W}\overset{\mathrm{O}}{\diagup\ \diagdown}\mathrm{W}$ bonds.

According to Wolfe and Newnham (*14*), Bi_2WO_6 shows a very polar, characteristic structure in which W is in a very distorted octahedral coordination. The lengths of the W–O bonds in Bi_2WO_6 are reported in Table 5. Bi_2WO_6 presents bonds with double bond character (d = 1.8 Å) and bonds with d = 2.3 Å, larger than d for the  $\mathrm{W}\overset{\mathrm{O}}{\diagup\ \diagdown}\mathrm{W}$ bonds.

We think that Bi_2WO_6 has no covalent bonds of the type  $\mathrm{W}\overset{\mathrm{O}}{\diagup\ \diagdown}\mathrm{W}$, in agreement with its polar structure, as suggested by Wolfe and Newnham (*14*). We attributed the band at 815 cm^{-1}, present in the ir spectrum of Bi_2WO_6, to W═O in agreement with our conclusion for Bi_2MoO_6 (*15*). The lower frequency at which W═O is present is due to the fact that these bonds are multiple. This agrees with what Cotton, Moorehouse and Wood (*16*) say for Mo compounds.

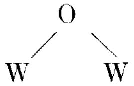
On the basis of the structural data of WO_3 and Bi_2WO_6 we attributed the isomerizing power at low temperature and the low selectivity at high temperature shown in oxidation of 1-butene by WO_3 to the covalent bonds of the type  $\mathrm{W}\overset{\mathrm{O}}{\diagup\ \diagdown}\mathrm{W}$. NH_3 increases the selectivity of propylene and butene, and this may be due to the fact that it reacts with  $\mathrm{W}\overset{\mathrm{O}}{\diagup\ \diagdown}\mathrm{W}$ thus impeding its interaction with olefines. W═O groups present in both Bi_2WO_6 and in WO_3 could be the surface sites responsible for the selective oxidation of 1-butene to butadiene in agreement with what was advanced for Bi molybdates (*17*).

In the opinion of Wolfe and Newnham (*14*), Bi tungstate 2/1 is ferroelectric. In its very distorted octahedral structure the W ion can move from the center of the octahedron and this displacement is typical of ferroelectric oxides. According to Orgel (*18*) the conditions under which an ion gives rise to a ferroelectric oxide are the same as those which allow the change of the ion from a distorted octahedral to a tetrahedral coordination in a reversible way, as both these coordinations are stable.

The ferroelectric nature of Bi tungstate 2/1 offers us the opportunity of broadening in this paper the concept of the double-bond role in oxidation catalysts. Orgel (*18*) suggests that the possibility that one ion can pass easily from one coordination to another is typical for an oxidation catalyst. In fact, he suggests that this property allows the removal of an oxygen from the catalyst with a low activation energy. In our opinion the presence of M–O bonds with double-bond character (as can be deduced from Orgel's paper) is one of the conditions that can lead to very distorted octahedra and therefore to the phenomenon of ferroelectricity. Therefore, considering Orgel's suggestions we can affirm that the presence of M–O bonds with double-bond character which in a past paper we had claimed to be a sign of catalytic activity (*17*) is so for following reasons:

i. the double bonds have a special reactivity in extracting hydrogen atoms from organic molecules (*17*, *19*).

ii. this process is facilitated by the fact that the ion can easily and in a reversible way change coordination. This possibility can decrease the activation energy for both the reduction of the double bond (in the moment in which it extracts hydrogen from organic molecules) and its reforming.

However, the presence in the bulk of the catalyst of W═O groups or of bonds of the type  $\mathrm{W}\overset{\mathrm{O}}{\diagup\ \diagdown}\mathrm{W}$ which can be observed through the ir or X-ray analysis, while being necessary are, nevertheless, not sufficient to render the catalyst an active one.

In fact we can offer no explanation for the inactivity of Bi_6WO_{12}, Bi_2O_3–$2WO_3$ and $Bi_2(WO_4)_3$ both in oxidation and ammoxidation reactions. Bi_2O_3–$2WO_3$(Bi–W 1/1 calcined at 500°C for 2 hr) is inactive although it has an absorption band at 890 cm^{-1} which is very probably due to W═O bonds. However, it showed the highest temperature of onset of bulk reduction with H_2 and therefore has a very low oxidation power.

$Bi_2(WO_4)_3$ (Bi/W 1/1 calcined at 600°C) is inactive or presents a very low activity. Despite this, it also presents both W=O bonds at 930 cm^{-1} and a temperature of onset of bulk reduction similar to the one of active catalysts of the WO_3 and Bi_2WO_4 type. However, $Bi_2(WO_4)_3$ catalyst extracted from the reactor after oxidation runs of 1-butene was green-blue in color (typical of tungsten bronzes) as if it had been irreversibly reduced.

Bi_2WO_6, Bi_2O_3–$2WO_3$ and Bi_6WO_{12} showed no modification in color after oxidation runs of 1-butene. Only WO_3 showed a little blue color. Bi_6WO_{12} showed the lowest temperature of onset of bulk reduction and has, therefore, a high oxidation power, but despite this it is inactive. This compound presents tungsten oxygen bonds with a very low degree of double-bond character. In fact the band at highest frequency in the ir spectrum (see Fig. 1) is at 800 cm^{-1}. This can be the reason for the lack of interaction with 1-butene according to what was reported earlier (*17*).

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