

Bismuth Carboxylates as Precursors for the Incorporation of Bismuth in Oxide-based Materials

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Received March 14, 1996; in revised form June 20, 1996; accepted June 20, 1996

The use of bismuth(III) carboxylates (acetate, oxoacetate, lactate, oxalate) as precursors for the incorporation of this element on oxide supports is evaluated as a new tool to generate bismuth-based oxide phases at the surface of MoO₃ or WO₃ supports. These insoluble precursors are deposited as small particles from a slurry in a liquid hydrocarbon under appropriate experimental conditions. Bismuth molybdate and tungstate phases are produced by solid-state reactions between *in situ* generated Bi₂O₃ and the supporting oxide at 673 K. The samples are characterized by specific surface area measurements, X-ray diffractometry, and X-ray photoelectron spectroscopy. The selective oxidation of isobutene to methacrolein is employed as a reaction test to demonstrate the applicability of this approach. The use of precursors containing lactate or acetate-type ligands is found to generate materials displaying enhanced specific surface area and high bismuth-to-molybdenum surface atomic ratios. This bismuth enrichment of the surface is indicative of the presence of dispersed crystallites of either Bi₂O₃ itself or ternary Bi–Mo–O or Bi–W–O phases, which are known to promote partial oxidation of alkenes. The performances of these materials in the isobutene to methacrolein conversion are indeed in most cases definitely better than those of the so-called reference materials obtained from the simple mixtures of the same oxides prepared separately. © 1996

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INTRODUCTION

Controlled pyrolysis of coordination compounds used as precursors for the synthesis of highly dispersed oxide-type materials generates growing interest in advanced research fields like superconductivity and thin film technology (1–3). The same approach can be applied to the preparation of complex multicomponent or multiphase supported catalysts in which the achievement of a well-defined local architecture is essential to control the cooperative

effects between the various partners. These synergetic effects have been extensively investigated in typical oxide-based catalysts for the selective oxidation of alkenes into aldehydes (4–7). Because the performances of such catalytic materials are directly related to the size of the oxide particles and to the interdispersion between the two oxides concerned, namely to the nature and extent of the contacts between the phases involved, well-defined preparation conditions are required. Within this frame, the choice of appropriate precursors and experimental methods for incorporating the catalytically active metals or promoters on the supporting phase is a critical step.

Multiphase supported catalysts are nowadays classically prepared by simultaneous precipitation of the various metals involved in the active phase. As far as bismuth and molybdenum are concerned, the methods are usually based on an impregnation procedure from highly acidic aqueous solutions of bismuth(III) nitrate and ammonium heptamolybdate. In these circumstances, the achievement of high dispersion levels is severely restricted by the differences in precursor–support interactions during the impregnation stage. These are the consequences of complex hydrolysis equilibria which give rise to various stoichiometries in the parent solution. In the frame of investigations on the hydrolysis products of bismuth(III) nitrate (8), species like Bi³⁺, BiO⁺, [Bi(OH)]²⁺, and [Bi(OH)₂]⁺ were shown to be accompanied by polycations such as [Bi₆O₄(OH)₄]⁶⁺, which seem to be the predominant species at pH values between 0.8 and 1.0. Similar phenomena may be invoked in the case of molybdenum, for which polyanionic species like [Mo₇O₂₄]⁶⁻ and [Mo₈O₂₆]⁴⁻ were shown to coexist at low pH values with numerous other species of lower nuclearity, depending on the molybdenum concentration (9). Differences in the ionic charges carried by these entities and in their molecular sizes modify the electrostatic interaction with the support and the accessibility of the potential adsorption sites for the precursor species. This precludes the adequate control of metal dispersion and was shown to be

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extremely critical in the case of carbon-supported molybdenum catalysts (10, 11).

The present work illustrates a different and original approach to the preparation of such materials, based on the *in situ* generation of Bi₂O₃ crystallites on the surface of another oxide acting as support (MoO₃ or WO₃). These attempts have as main objective to create and maximize the interfacial connection between Bi₂O₃ and MoO₃ or WO₃, favoring, thereby, either the formation of a new interfacial Bi–Mo–O or Bi–W–O phase or the manifestation of cooperative effects between the two oxides by increasing and improving the contacts between them.

Carboxylate-type precursors were chosen because they are known to undergo thermal degradation under mild conditions ($T < 673$ K), i.e., at temperatures which are lower than or comparable with the operating temperature selected for usual catalytic tests in gas phase (in the range 673–773 K). The activation step which converts the precursor into a catalytically active phase therefore eliminates the occurrence of a more extensive sintering effect than that resulting merely from the normal operating conditions and limits the extent of solid state reactions. A further advantage that these compounds offer for that purpose lies in the fact that only carbon, hydrogen, and oxygen atoms are present in the starting material: poisoning problems commonly associated with the presence of other heteroatoms like sulfur or halogens on the catalyst surface, when other precursor salts are used, are consequently avoided.

Several carboxylate-type compounds, which differ from the point of view of their substituents and side functionalities, were selected as precursors in the present work: two monocarboxylates (Bi(III) triacetate and oxoacetate), one α -hydroxycarboxylate (dilactate complex), and one dicarboxylate (oxalate complex). All these compounds are easily converted into α -Bi₂O₃ when heated at temperatures in the range 573–673 K. At these temperatures, further solid-state reactions between *in situ* generated Bi₂O₃ and MoO₃ or WO₃ may give rise, at least partially, to various catalytically active bismuth molybdate or tungstate phases. The precursors are deposited in the form of small particles, from a suspension in an aliphatic hydrocarbon liquid, like *n*-heptane, in which they are not soluble.

According to this procedure, the nature and structure of the bismuth precursor and the oxide supports are preserved up to the calcination step. During their subsequent thermal decomposition, the precursor particles will hopefully develop a large surface area, thus creating in principle the most favorable conditions for an efficient phase interaction or cooperation between the supported phase and the support. To evaluate the actual potential of this preparation route, the catalytic properties of the obtained materials were compared to those of reference catalysts prepared

TABLE 1
Decomposition Temperature of Bi(III) Carboxylates into α -Bi₂O₃ under Isothermal Conditions and BET Specific Surface Area of the Resulting Oxide

Precursor ^a	T (K)	S_{BET}^b (m ² ·g ⁻¹)
BiO(OAc)	613	0.57
Bi(OAc) ₃	613	0.52
Bi(lact) ₂	563	0.43
Bi ₂ Ox ₃	538	0.40
Bi(Hcit)	613	0.78
Bi(prop) ₃	633	1.58

^a OAc = acetate; lact = lactate; Ox = oxalate; Hcit = citrate (O₂C-C(OH)(CH₂CO₂)₂); prop = propionate.

^b Specific surface area of powder Bi(III) oxide prepared by calcination of the carboxylate at 673 K for 20 h.

from mechanical mixtures of the support with pure Bi₂O₃ instead of the bismuth carboxylate precursor.

The objective of the present paper is to report on first observations concerning the applicability of this approach to materials preparation, by showing that it is indeed possible to “decorate” MoO₃ or WO₃ with tiny bismuth-containing crystallites, and that the high reactivity of Bi₂O₃ with these oxides leads to the formation of active “Bi–Mo–O” or “Bi–W–O” phases.

EXPERIMENTAL

Synthesis of the Bismuth-containing Precursors

The various precursors selected in this work were respectively the triacetate Bi(CH₃CO₂)₃ (noted Bi(OAc)₃), the oxoacetate BiOCH₂CO₂ (noted BiO(OAc)), the dilactate Bi(C₃H₄O₃)(C₃H₅O₃) (noted Bi(lact)₂), and the oxalate Bi₂(C₂O₄)₃ (noted Bi₂Ox₃), all in their anhydrous form. Published literature procedures were used for the synthesis of Bi(OAc)₃ (12) and the heptahydrated oxalate Bi₂Ox₃·7H₂O (13). The anhydrous oxalate was obtained by dehydration of the latter at 473 K. Anhydrous Bi(III) dilactate was produced similarly at 498 K. Detailed accounts on the synthetic procedures and physico-chemical characterization (IR, XRD, thermal behavior) of these and related compounds in view of their use as precursors for α -Bi₂O₃ are reported elsewhere (14). The temperatures at which these carboxylate precursors can be quantitatively degraded into α -Bi₂O₃ are listed in Table 1, together with the data on some related compounds. This table also gives some indications on the BET specific surface area of the

powdered Bi_2O_3 samples obtained by calcination of these various carboxylates in air at 673 K for 20 h.

Supports

Two oxides were used as supporting materials: MoO_3 and WO_3 .

(a) MoO_3 : Samples of molybdenum (VI) oxide of different specific surface areas were obtained as following:

—from calcination of ammonium heptamolybdate at 773 K during 20 h, resulting in a specific surface area of about $1.9 \text{ m}^2 \cdot \text{g}^{-1}$;

—by the citrate method: the citrate complex was prepared from an aqueous solution of ammonium heptamolybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{ H}_2\text{O}$ (Janssen, 99%, 0.2 mol/liter) and citric acid (Merck, 99%, 1.6 mol/liter). Once a clear solution is obtained, water is driven off under vacuum and the mixture is converted into an homogeneous gel, which is dried upon vacuum heating for 20 h at 363 K. The collected dark-blue cake is ground into a finely dispersed powder and heated at 573 K for an additional 20-h period. The molybdenum precursor was calcined at 673 K for 20 h, producing MoO_3 with an average specific surface area of $1.9 \text{ m}^2 \cdot \text{g}^{-1}$;

—by the oxalate method: the oxalate precursor was synthesized like in the citrate method from an aqueous solution of ammonium heptamolybdate (0.2 mol/liter) and oxalic acid (UCB, 99.5%, 1.7 mol/liter). After evaporation and drying at 353 K for 20 h, the complex is thermally degraded upon heating at 573 K for 20 h. Calcination of this precursor at 773 K during 20 h produces MoO_3 characterized by a specific surface area of about $3.2 \text{ m}^2 \cdot \text{g}^{-1}$.

(b) WO_3 : Tungsten (VI) oxide (UCB) with a BET specific surface area of $4.2 \text{ m}^2 \cdot \text{g}^{-1}$ was used as received.

Preparation of the Supported Materials

Bismuth loading. To validate the present approach, it is necessary to avoid that the coating of the supporting oxide phase by the deposited phase be so extensive that it prevents the access of reactants to the former; consequently, the promoting element, bismuth, is incorporated at a low loading of 2 wt% Bi_2O_3 . Using crystallographic parameters determined by Malmros (15), the projected area of $\alpha\text{-Bi}_2\text{O}_3$ can be estimated to be 14.10^{-20} m^2 . The corresponding weight percentage of bismuth oxide necessary to give a formal monolayer coverage on an oxide support exhibiting a specific surface area of $1 \text{ m}^2 \cdot \text{g}^{-1}$ is found to be $0.55 \text{ wt\%} \cdot \text{m}^{-2}$. Based on the highest value of specific surface area of the supports used in this work ($4.2 \text{ m}^2 \cdot \text{g}^{-1}$), a standard value of 2 wt% Bi_2O_3 has been selected for all the preparations. This corresponds *formally* (i.e., assuming perfect dispersion) to about one monolayer in the case of MoO_3 with $3.2 \text{ m}^2 \cdot \text{g}^{-1}$ and WO_3 with $4.2 \text{ m}^2 \cdot \text{g}^{-1}$ and two monolayers in the case of MoO_3 with $1.9 \text{ m}^2 \cdot \text{g}^{-1}$.

Unless complete spreading would take place, we would therefore hopefully preserve the accessibility to most of the MoO_3 or WO_3 after the formation of the Bi_2O_3 crystallites on these oxides.

Because such a low value does not allow one to identify easily the solid phases present in the catalyst by powder X-ray diffractometry, a few samples were prepared using three times the amount of bismuth precursors (6 wt% Bi_2O_3).

Multiphasic catalytic materials: Mixed Bi–Mo and Bi–W supported oxides. Supported materials were prepared by incorporating the bismuth-containing precursor on the surface of the oxide support, according to a deposition method from a slurry of the carboxylate in *n*-heptane. Because it is essential to retain the structure of the selected precursors on the support up to the calcination stage, suitable handling and sampling conditions able to warrant their stabilization were strictly respected. More particularly, most of the operations were conducted under an atmosphere of dry nitrogen to prevent hydrolysis of the Bi(III) compounds.

(a) Starting from carboxylate precursors: the Bi(III) carboxylate and the supporting oxide were carefully put in contact in the hydrocarbon, while avoiding any modification of them during the mixing process. The appropriate amount of bismuth carboxylate was first dispersed at room temperature in 100 ml *n*-heptane under ultrasonic stirring for 15 min; after addition of the oxide support (about 5 g of MoO_3 or WO_3) to this suspension and further sonication for the same time, the hydrocarbon was evaporated very slowly at room temperature under vacuum and continuous stirring. In the case of bismuth triacetate, the former procedure was carried out under a dry nitrogen atmosphere to prevent hydrolysis of this highly water-sensitive compound.

The supported materials are denoted as $\text{MO}_3/A/L$ in which *M* is Mo or W, *A* is the surface area of the oxide support, and *L* is the type of precursor as described above.

(b) Pure MoO_3 , WO_3 , or $\alpha\text{-Bi}_2\text{O}_3$ oxides were used as blank samples for comparison to the catalytic performances of the supported oxides.

(c) Reference supported oxides were prepared by using $\alpha\text{-Bi}_2\text{O}_3$ (VENTRON, 99.8%) itself instead of one of the bismuth-containing precursors. Bismuth oxide was introduced either as a mechanical mixture according to the deposition procedure described above, or merely by dry grinding with the partner oxide in the absence of heptane. The corresponding supported oxides are noted in the form $\text{MO}_3/A/\text{Bi}_2\text{O}_3$ (Disp) and $\text{MO}_3/A/\text{Bi}_2\text{O}_3$ (Grind), respectively, in which *M* is Mo or W, *A* is the BET specific surface area of MO_3 , Disp refers to the dispersion procedure in organic medium described above, and Grind refers to the dry grinding procedure.

All the supported samples were calcined at 673 K in air

for 20 h before their use in comparative catalytic tests. This temperature is high enough to promote the decomposition of the Bi-containing precursor and the formation of mixed Bi–Mo–O or Bi–W–O phases, without substantial loss of specific surface area.

Pure Bi₂O₃ and bismuth molybdate phases. Pure Bi₂O₃ and bismuth molybdate phases were prepared independently and used as reference samples for the XPS analysis.

Several Bi₂O₃ samples were obtained from thermal degradation of Bi(III) carboxylates (acetate, propionate, citrate) in air at 673 K, or Bi(III)nitrate at 773 K. The various molybdate phases, α -Bi₂Mo₃O₁₂, β -Bi₂Mo₂O₉, and γ -Bi₂MoO₆ were obtained from calcination of Bi(III) and Mo(II) acetates mixed in appropriate amounts (dry grinding under argon), at 673 K for the α - and γ -phases, and at 923 K for the β -phase (16).

Evaluation of the Catalytic Performances

Because the solid-state characteristics of these materials play a prominent role in their catalytic behavior, selected samples were submitted to a standard catalytic test under the same reaction conditions, in order to provide some indirect evidence that would help in evaluating the present approach to materials synthesis.

The selective oxidation of isobutene into methacrolein using air at 693 K was selected as catalytic test reaction. Half a gram of catalyst (particle size 0.5–0.8 mm) was used for each run. Reagents (total flow rate of 32 ml·min⁻¹) were introduced as a mixture made up of 90.6 vol.% air and 9.4 vol.% isobutene.

The composition of the gaseous mixture at the reactor output was quantitatively analyzed with a gas chromatograph INTERSMAT IGC 12M equipped with two 2.5-m-long analytic columns, one for the analysis of methacrolein (stationary phase TENAX) and the other for the separation of isobutene, CO₂, and H₂O (stationary phase PORA-PAK Q). Helium was used as carrier gas and detection was made by catharometry. Side products were CO, CO₂, and small amounts of acrolein.

Catalytic results are expressed by means of the following three parameters: conversion (X , %), representing the total percentage of isobutene transformed; yields (Y , %), namely methacrolein moles reported to the initial isobutene moles fed into the catalytic bed; and selectivities (S , %), calculated from the equation $S = 100(Y/X)$. The reported values are related to the stationary state after running 1 h at the given temperature.

Characterization Techniques

Specific surface area. BET specific surface area measurements are carried out on a MICROMERITICS ASAP 2000 apparatus using krypton at 77 K. Samples are previously outgassed under vacuum at 423 K. The experimen-

tal data are treated using a cross-sectional area of 0.20 nm² for the Kr atoms.

XRD. Powder X-ray diffraction patterns are obtained with a SIEMENS 500 diffractometer equipped with a copper anode.

XPS. X-ray photoelectron spectroscopy is performed on a SSI-100 Model 206 spectrometer of Surface Science Instruments, using the AlK α radiation ($E = 1486.6$ eV). The energy scale is calibrated by taking the Au 4f_{7/2} binding energy at 84.0 eV. The C_{1s} binding energy of contamination carbon fixed at 284.8 eV is used as internal standard value. The analysis of bismuth, molybdenum, and tungsten are based on the following photopeaks, respectively: Bi(4f_{7/2}), Mo(3d_{5/2}), and W(4f_{7/2}). For the analysis of the tungsten photoelectron spectra, the difference ΔE_b between the binding energies of the 4f_{7/2} and 4f_{5/2} electronic sublevels is taken at 2.15 eV (17), with an intensity ratio $I(4f_{7/2})/I(4f_{5/2})$ fixed at 1.33. Relative surface concentrations are calculated by comparing with SiO₂ used as external reference.

RESULTS

Characterization of the Supported Oxides

S_{BET}. Specific surface area values of catalysts are listed in Table 2. For all the samples in which Bi₂O₃ is generated *in situ* by the carboxylate route, these values are found to be systematically larger than those of the pure support. It is furthermore worth noting that, when pure MoO₃ is submitted to the treatment used for the preparation of mechanical mixtures, i.e., sonication in *n*-heptane, its specific surface area remains perfectly unchanged. The most significant variations in specific surface area are observed in the case of Bi₂Ox₃ and Bi(OAc)₃ on MoO₃/3.2 m²·g⁻¹, for Bi(lact)₂ on MoO₃/1.9 m²·g⁻¹, and for Bi(OAc)₃ on WO₃/4.2 m²·g⁻¹. On the contrary, when Bi₂O₃ is introduced as such on the support by mechanical mixing (Disp or Grind samples), there is definitely no significant change of the BET specific surface area. The extensive increases in the surface areas observed in the other samples are therefore clearly related to the generation of Bi₂O₃ *in situ* from the various carboxylate precursors.

XRD spectra. Pure and supported oxides were submitted to powder X-ray diffractometry before and after their use in catalytic tests. Specific Bi-loaded phases were not detectable in most of the supported materials containing 2 wt% Bi. As far as the support is concerned, the comparison of XRD data collected on untreated and loaded samples, after precursor deposition and calcination, confirms that peaks related to the molybdenum or tungsten oxide phases remain unchanged, showing that the bulk of the main oxide component is not altered by the successive preparation steps.

TABLE 2
Selected BET and XPS Results

Supported oxides support/ S_{BET} ($\text{m}^2\cdot\text{g}^{-1}$)/precursor	Bismuth precursor ^{a,b}	S_{BET} ($\text{m}^2\cdot\text{g}^{-1}$)		$\frac{\text{Bi}}{\text{M}} * 100^d$
		Pure support	Catalyst ^c	
MoO ₃ /1.9/BiO(OAc)	BiO(OAc)	1.9	4.1	3.4
MoO ₃ /1.9/Bi(OAc) ₃	Bi(OAc) ₃	1.9	—	1.9
MoO ₃ /1.9/Bi(lact) ₂	Bi(lact) ₂	1.9	4.7	2.4
MoO ₃ /1.9/Bi(lact) ₂ (6%)	Bi(lact) ₂ -6%	1.9	5.6	5.8
MoO ₃ /1.9/Bi ₂ Ox ₃	Bi ₂ Ox ₃	1.9	—	0.24
MoO ₃ /1.9/Bi ₂ O ₃ (Grind) ^f	—	1.9	1.8	0.0 ^e
MoO ₃ /1.9/Bi ₂ O ₃ (Disp) ^g	—	1.9	2.2	0.0 ^e
MoO ₃ /3.2/BiO(OAc)	BiO(OAc)	3.2	—	1.0
MoO ₃ /3.2/Bi(OAc) ₃	Bi(OAc) ₃	3.2	6.0	3.0
MoO ₃ /3.2/Bi(lact) ₂	Bi(lact) ₂	3.2	—	1.1
MoO ₃ /3.2/Bi ₂ Ox ₃	Bi ₂ Ox ₃	3.2	11.4	0.3
WO ₃ /4.2/BiO(OAc)	BiO(OAc)	4.2	7.2	0.9
WO ₃ /4.2/Bi(OAc) ₃	Bi(OAc) ₃	4.2	9.7	5.4
WO ₃ /4.2/Bi(lact) ₂	Bi(lact) ₂	4.2	6.1	—
WO ₃ /4.2/Bi ₂ Ox ₃	Bi ₂ Ox ₃	4.2	6.3	1.8
WO ₃ /4.2/Bi ₂ O ₃ (Grind) ^f	—	4.2	4.7	0.0 ^e
WO ₃ /4.2/Bi ₂ O ₃ (Disp) ^g	—	4.2	4.5	0.0 ^e

^a 2 wt.% Bi₂O₃, unless otherwise stated.

^b OAc = acetate; Ox = oxalate; lact = lactate.

^c After deposition and calcination of the precursor at 673 K for 20 h.

^d M-Mo or W; surface intensity ratio determined by XPS using the following peaks: Bi ($4f_{7/2}$), Mo ($3d_{5/2}$), W ($4f_{7/2}$) (before use in catalytic tests). Bulk value is 1.2%.

^e Bismuth was not detected by XPS.

^f Mechanical mixture.

^g Dispersion in organic solvent.

In the diffraction pattern of a supported oxide loaded with 6 wt% Bi from the lactate complex, the presence of α -bismuth molybdate Bi₂Mo₃O₁₂ together with small amounts of γ -Bi₂MoO₆ is non equivocal (Fig. 1). The Bi₂Mo₃O₁₂ phase is also revealed by a closer look at the data corresponding to the Bi–Mo catalyst made from 2 wt% bismuth lactate.

XPS measurements. The binding energy values range respectively between 159.4 and 160.2 eV for Bi $4f_{7/2}$ and between 232.6 and 233.4 eV for Mo $3d_{5/2}$. There is no significant change after their use in the catalytic tests. The values observed for the Bi component are slightly larger than those reported in the literature (158.8 (18) and 159.3 eV (19)) or those measured with the same equipment for various α -Bi₂O₃ samples made from different Bi(III) precursors, carboxylates, or nitrate (see Table 3: E_b values in the range 158.9 ± 0.2 eV). According to the literature, corresponding values for Bi in bismuth molybdates lie within the range 158.5–159.0 eV (18, 20). The experimental values observed in bismuth molybdate reference samples prepared from the mixture of Bi(III) and Mo(II) acetates

appear however to be slightly larger (Table 3) and closer to those measured in the catalysts. On the other hand, the E_b values characterizing the Mo component are in line with those mentioned in literature either for molybdenum(VI) oxide (E_b (Mo $3d_{5/2}$) = 232.6 ± 0.2 eV (21–23)) or for the various bismuth molybdates (E_b = 231.8–232 eV (18, 20)). Although the coexistence of the binary oxide Bi₂O₃ and a ternary Bi–Mo–O phase corresponding to one or several bismuth molybdate components cannot be totally excluded, the present XPS results seem to support the formation of bismuth molybdates on the surface, in agreement with the XRD data described above.

Similar conclusions can be drawn from the decomposition of the W $4f$ photoelectron spectra into two doublets (I and II, Fig. 2) characterized by the following E_b values: E_b ($4f_{7/2}$) = 34.8 (I) and 36.0 (II) eV; E_b ($4f_{5/2}$) = 37.0 (I) and 38.1 (II) eV. Component I can be assigned to the main component, namely WO₃ (E_b ($4f_{7/2}$) = 35.4–35.9 eV (24–26)), while component II should be compatible with a Bi tungstate-type phase (E_b ($4f_{7/2}$) = 35.8–36.7 eV in Al₂(WO₄)₃ (24–26)). An analogous deconvolution of tung-

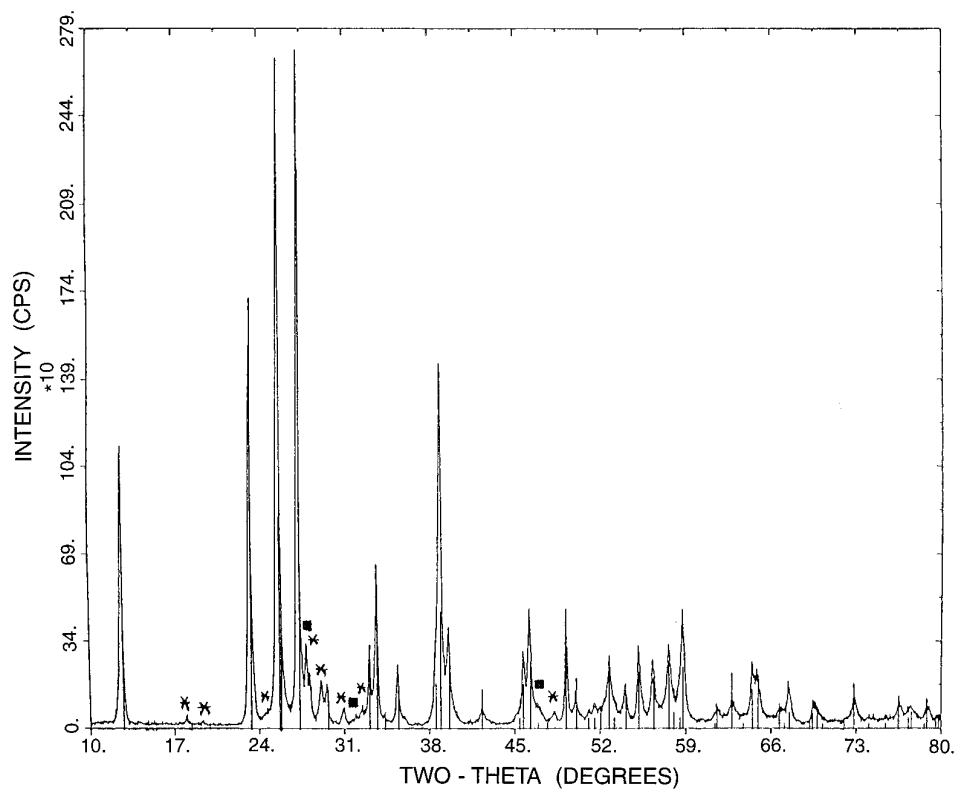


FIG. 1. X-ray powder diffractogram of $\text{MoO}_3/1.9/\text{Bi}(\text{lact})_2$ (6 wt.%) Vertical lines correspond to MoO_3 . Ternary oxide phases are labeled with asterisks ($\alpha\text{-Bi}_2\text{Mo}_3\text{O}_{12}$) and squares ($\gamma\text{-Bi}_2\text{MoO}_6$).

TABLE 3
XPS Characterization of Pure Bi_2O_3 and Bismuth Molybdates Prepared by Calcination of Carboxylates

Compound	Precursor ^a	T_{calc}^b (K)	Binding energy (eV)			XPS atomic intensity ratios			
			O1s ^c	Bi4f _{7/2}	Mo3d _{5/2}	C/Bi	O(I)/Bi	Bi/Mo	O(I)/Mo
$\alpha\text{-Bi}_2\text{O}_3$	^d	—	531.7 (Ia) 529.9 (Ib)	159.1	—	1.3	1.7	—	—
$\alpha\text{-Bi}_2\text{O}_3$	$\text{Bi}(\text{OAc})_3$	673	531.1 (Ia) 529.5 (Ib)	158.8	—	1.2	1.5	—	—
$\alpha\text{-Bi}_2\text{O}_3$	$\text{Bi}(\text{prop})_3$	673	531.2 (Ia) 529.6 (Ib)	158.9	—	1.0	1.6	—	—
$\alpha\text{-Bi}_2\text{O}_3$	$\text{Bi}(\text{Hcit})$	673	531.1 (Ia) 529.5 (Ib)	158.7	—	1.1	1.6	—	—
$\alpha\text{-Bi}_2\text{O}_3$	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	773	531.2 (Ia) 529.5 (Ib)	158.9	—	1.0	1.6	—	—
$\gamma\text{-Bi}_2\text{MoO}_6$	$\text{Bi}(\text{OAc})_3 + \text{Mo}_2(\text{OAc})_4$	773	532.1 (II) 530.2 (I)	159.3	232.5	1.8	3.8	1.6	6.2
$\beta\text{-Bi}_2\text{Mo}_2\text{O}_9$	$\text{Bi}(\text{OAc})_3 + \text{Mo}_2(\text{OAc})_4$	893	532.3 (II) 530.6 (I)	159.6	232.6	2.9	4.7	1.1	5.2
$\alpha\text{-Bi}_2\text{Mo}_3\text{O}_{12}$	$\text{Bi}(\text{OAc})_3 + \text{Mo}_2(\text{OAc})_4$	773	532.7 (II) 530.5 (I)	159.5	232.7	3.1	8.0	0.6	4.7

^a OAc = Hcit = citrate; prop = propionate.

^b Calcination temperature (air, 20 h).

^c Components Ia and Ib in Bi_2O_3 are ascribed to oxide and OH groups, components I and II in molybdates, to oxide and C–O contamination, respectively.

^d Commercial Bi_2O_3 purchased from VENTRON.

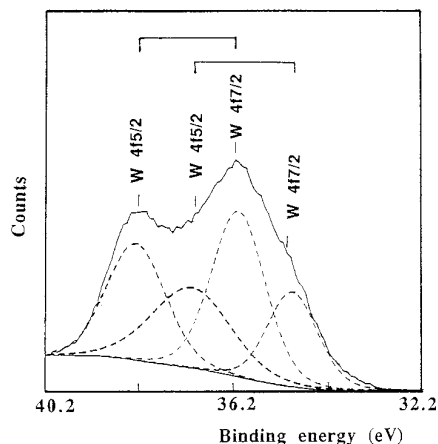


FIG. 2. W 4f photoelectron spectrum of $\text{WO}_3/4.9/\text{Bi}(\text{OAc})_3$.

sten oxide XPS spectra has been described in the frame of studies on the formation of WO_3 layers on the surface of dispersed silica (27); the higher energy component ($E_b = 37.2$ eV) was assigned to tungsten oxide layers which are involved in strong chemical interaction with the silica support.

A few additional comments can be formulated on the basis of the relative intensities of the photoelectron peaks (Table 2). The Bi-to-Mo ratios have to be compared with the "bulk" value of 1.2% corresponding to the selected Bi loading (2 wt% Bi_2O_3). Whereas most of the samples prepared from bismuth carboxylates were shown to give high Bi-to-Mo ratios, the use of oxalate as precursor is associated with a very low Bi/M value, suggesting the incorporation of bismuth in large crystals aside the smaller particles of the supporting oxide.

The C 1s photopeaks, as observed before performing the catalytic tests, are perfectly symmetrical whatever the precursor used, and their binding energies are identical to those typically accepted for contaminating hydrocarbon. As indicated in Table 3, the residual amount of carbon in Bi_2O_3 samples prepared by the carboxylate route is very low and similar to that observed after calcination of Bi(III) nitrate at 773 K. No significant amounts of carbon are therefore produced by the use of these carboxylate-type precursors.

Catalytic Performances

Selected catalytic results obtained at 693 K are listed in Table 4. Pure MoO_3 and WO_3 are both known as active but nonselective phases in oxidation of isobutene. Pure bismuth oxide does not display any significant catalytic activity for the examined reaction and produces only CO_x . Although the selectivities in methacrolein remain low, these catalytic results provide valuable information that can be correlated with the physico-chemical characteristics.

TABLE 4
Measurement of the Catalytic Performances in the
Isobutene–Methacrolein Conversion at 693 K

Supported oxide ^{a,b} support/ S_{BET} ($\text{m}^2\cdot\text{g}^{-1}$)/Precursor	X^c (%)	Y^d (%)	S^e (%)
$\text{MoO}_3/1.9/-$	77.8	9.8	12.6
$\text{MoO}_3/1.9/\text{Bi}(\text{OAc})_3$	73.6	10.3	14.0
$\text{MoO}_3/1.9/\text{Bi}_2\text{Ox}_3$	71.3	2.8	4.0
$\text{MoO}_3/1.9/\text{Bi}(\text{lact})_2$	83.6	14.9	17.9
$\text{MoO}_3/1.9/\text{Bi}_2\text{O}_3(\text{Grind})^f$	68.6	3.4	5.0
$\text{MoO}_3/1.9/\text{Bi}_2\text{O}_3(\text{Disp})^g$	67.8	3.5	5.2
$\text{WO}_3/4.2/-$	53.2	2.1	4.0
$\text{WO}_3/4.2/\text{Bi}(\text{OAc})_3$	64.3	5.5	8.6
$\text{WO}_3/4.2/\text{Bi}_2\text{Ox}_3$	45.6	1.3	2.9
$\text{WO}_3/4.2/\text{Bi}(\text{lact})_2$	51.8	2.8	5.4
$\text{WO}_3/4.2/\text{Bi}_2\text{O}_3(\text{Grind})^f$	50.4	1.9	3.8
$\text{WO}_3/4.2/\text{Bi}_2\text{O}_3(\text{Disp})^g$	50.2	2.0	4.0
Bi_2O_3^h	9.0	0.0	0.0

^a 2 wt.% Bi_2O_3 on the support.

^b OAc = acetate; Ox = oxalate; lact = lactate.

^c Total isobutene conversion.

^d Yield in methacrolein.

^e Selectivity in methacrolein.

^f Mechanical mixture.

^g Dispersion in organic solvent.

^h Bi_2O_3 alone (500 mg); for lower amounts, no activity is observed (28).

When comparing the performances of the pure oxide supports with those of the bimetallic catalysts made from a carboxylate-type bismuth precursor on the same oxide support, the two main comments are the following:

(i) Supported oxides prepared from acetate and lactate precursors exhibit fairly significant effects on both the yield and selectivity. Those made from bismuth oxalate (Bi_2Ox_3) show lower conversion, yield, and selectivity.

(ii) Compared with bimetallic catalysts prepared with acetate or lactate ligands, reference supported oxides prepared directly from Bi_2O_3 itself instead of its carboxylate-type precursors show systematically lower conversion, yield, and selectivity. This result is independent from the way in which bismuth oxide and molybdenum or tungsten oxide are put in contact (dry grinding or dispersion in *n*-heptane).

DISCUSSION

As shown in Table 1, Bi_2O_3 samples prepared from carboxylate precursors exhibit specific surface areas in the range $0.5\text{--}1.6$ $\text{m}^2\cdot\text{g}^{-1}$, i.e., significantly higher than commercially available Bi_2O_3 (about 0.2 $\text{m}^2\cdot\text{g}^{-1}$). Consequently, the considerable increase in specific surface area observed when the pure MoO_3 or WO_3 supports are calcined in the presence of the bismuth carboxylate precursor

suggests several comments. When the additional specific surface areas ($(S_{\text{BET}})_{\text{Bi-M-O}} - (S_{\text{BET}})_{\text{pure support}}$) are ascribed to the actual deposited amount of bismuth oxide (2 wt%), the obtained specific surface areas exceed by far those measured on pure Bi_2O_3 powder samples prepared from the corresponding precursors. However, the observed increase in the specific surface areas could also be ascribed to the production of residual carbon coming from the carboxylate precursors. Detailed XPS investigations performed on pure Bi_2O_3 samples made from carboxylate precursors (Table 3) allow us to rule out this assumption, at least in the case of the acetate precursor or similar short-chain carboxylates. The alternative interpretation that the ultrasonic treatment would smash the support to fragments during the deposition procedure must also be discarded because, as mentioned earlier, there is no increase in BET specific surface area when the support is submitted to the standard treatment applied to the mechanical mixtures. In addition, the catalytic performances of pure molybdenum oxide submitted or not to ultrasonic waves were found to be similar. It can therefore be concluded that the most reasonable explanation for the increase of the specific surface areas in the Bi-loaded catalysts made via the carboxylate route seems to be the formation of small crystallites of the ternary oxide phases Bi-Mo-O and Bi-W-O as a consequence of solid-state reactions occurring between *in situ* generated Bi_2O_3 and the corresponding pure oxide, MoO_3 or WO_3 . The simultaneous presence of crystallites of unreacted Bi_2O_3 on the surface can nevertheless not be excluded.

When considering the surface areas listed in Table 2, it is obvious that the observed enhancement in conversion, yield, and selectivity cannot be merely ascribed to an increase of the catalytically active surface, indicating that other phenomena, most probably related to the nature of the precursors, are directly involved in the increase of the performances.

When analyzed in the light of the XPS and BET measurements, the catalytic performances themselves suggest the following conclusions:

(a) In all cases, MoO_3 -supported oxides prepared using acetate or lactate precursors show a higher conversion, yield, and selectivity than those obtained directly from Bi_2O_3 itself. This observation strengthens the assumption that the control of both the nature of the active phase and of bismuth dispersion are better achieved when Bi_2O_3 is generated *in situ* from carboxylic precursors.

(b) The highest value for the selectivity in methacrolein is observed when bismuth lactate is used as precursor on MoO_3 . As shown in Table 2, the sample $\text{MoO}_3/1.9/\text{Bi}(\text{lact})_2$ displays an important increase (147%) in specific surface area, together with a high Bi/Mo ratio (2.4%, i.e., twice the bulk value of 1.2%), as observed in XPS. The XRD results suggest the presence in this sample of a mixture

of α - and γ -bismuth molybdates. These two phases are characterized by a significantly different catalytic behavior and it is well recognized that they can cooperate as two separate phases during the selective oxidation of propene or isobutene in acrolein or methacrolein (7, 29, 30). These results suggest that the observed selectivity enhancement might be related to the formation of ternary oxide phases in the supported catalysts, and that the effect is more pronounced when carboxylate precursors are used, due to a better interdispersion of the ternary oxide phases formed. Once again, this statement does not allow us to rule out the presence of Bi_2O_3 on the surface. The question whether this binary oxide can also play a role in increasing selectivity remains open. When used alone, Bi_2O_3 is known as nonselective for partial oxidation products but, as mentioned earlier, this oxide can promote the catalytic behavior of other binary or ternary oxide phases. The exact role played by Bi_2O_3 in our samples falls beyond the scope of the present work.

(c) Compared with MoO_3 , WO_3 itself is known to be a poorer catalyst for the selective oxidation of alkenes. The bismuth-containing WO_3 samples exhibit much lower activities than the corresponding MoO_3 -supported samples. A similar trend as in MoO_3 -based catalysts is however observed when the influence of the precursor nature is investigated. Although the absolute performances remain very low, when compared with pure WO_3 , the sample $\text{WO}_3/4.2/\text{Bi}(\text{OAc})_3$ displays a significant positive effect, with yield and selectivity values in methacrolein that are doubled with respect to the unloaded support. Here again, this oxide is characterized by a high Bi/W ratio in XPS and simultaneously shows a pronounced increase (100%) of its specific surface area (Table 2).

(d) MoO_3 - or WO_3 -supported oxides made from bismuth oxalate exhibit very poor catalytic performances. The low Bi-to-M ratio observed in XPS (Table 2) actually suggests that, when oxalate is used, the incorporation method fails in ensuring an homogeneous dispersion of this precursor during the loading step. The catalytic behavior of these samples might be due to the formation of bigger Bi_2O_3 crystallites on the surface, decreasing the contacts with the support and inhibiting thereby the formation of the ternary oxides which are thought as responsible for the enhanced selectivity. As discussed above, the presence of pure, isolated Bi_2O_3 gives rise to nonselective sites which are responsible for lower performances than the corresponding pure supports.

To summarize, the characteristics and performances of the samples prepared via the carboxylate route give signs that the dispersion of the active phases on the surface is facilitated by this procedure: samples characterized by higher Bi/Mo atomic intensity ratios in XPS, indicating bismuth enrichment on the surface, display high specific surface areas and give rise, simultaneously, to improved

catalytic performances for the partially oxygenated product. This was clearly not the case in samples made from calcination of mechanical mixtures of the concerned binary oxides $\text{Bi}_2\text{O}_3\text{-MO}_3$ ($M = \text{Mo}, \text{W}$). Mixed ternary phases are formed by incorporation of bismuth in the lattices of MoO_3 or WO_3 , but some crystallites of small or larger size are most probably formed also. The improvement in the catalytic performances could then be due either to the presence of these ternary phases or to cooperation effects between the coexistent phases. More precise explanations for the enhanced catalytic performances are outside the scope of this study.

CONCLUSIONS

From a methodological point of view, this work suggests that the use of bismuth carboxylates as precursors for the incorporation of this element in multiphasic oxide-based materials provides an interesting procedure to generate bismuth(III) oxide and subsequently bismuth molybdates or tungstates at the surface of MoO_3 or WO_3 supports.

Using the selective oxidation of isobutene to methacrolein as a reaction test to evaluate the potentialities of this new approach, improved catalytic performances for partial oxidation are observed in most cases when compared with samples made directly from mechanical mixture of the corresponding oxides. These effects seem to be correlated with the type of phase formed at the surface and the dispersion level which is achieved for bismuth on the supporting oxide.

Despite the great similarity between the carboxylates selected as precursors in these experiments, the type of phase formed and their dispersion depend on the nature of the carboxylate group and the stoichiometry of the compound. These preliminary results indicate that this approach can be evaluated as a promising tool to modulate the architecture of supported oxides, and strongly suggest it will be fruitful to expand this methodology by extending the range of precursors and supports investigated.

ACKNOWLEDGMENTS

The authors greatly acknowledge financial assistance from the Belgian National Fund for Scientific Research, Brussels, and from the "Ministère de la Région Wallonne," Belgium, in the frame of a Concerted Action. This work was supported by fellowships allotted by the CONICET and

the National University of San Luis, Argentina (L.E.C.) and by the "Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture," Belgium (O.T.).

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