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New insights in the understanding of the behaviour and performances of bismuth molybdate catalysts in the oxygen-assisted dehydration of 2-butanol

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Abstract

Pure $Bi_2Mo_3O_{12}$, $Bi_2Mo_2O_9$, Bi_2MoO_6, MoO_3 and α-Sb_2O_4 and their mechanical mixtures were investigated in the oxygen-assisted dehydration of 2-butanol at atmospheric pressure and at low temperature (220 and 250°C). All catalysts were characterized before and after the catalytic reaction by BET surface area measurement, Raman spectroscopy, XRD and XPS. A strong parallelism is confirmed with the results obtained in the selective oxidation of olefins. In the frame of the remote control concept, α, β and γ-bismuth molybdates are able to play a dual role: donor of spillover oxygen (Oso) with respect to MoO_3, and acceptor of Oso with respect to α-Sb_2O_4. On one hand, this duality leads to mutual increase of activity when the bismuth molybdates are mixed together. In the presence of MoO_3, the α phase seems to be a stronger Oso donor than β and γ, and β has a donor strength between α and γ. On the other hand, when the Bi molybdates are reacted in the presence of a big quantity of spillover oxygen, like in a mixture with α-Sb_2O_4, they undergo a dramatic decrease of activity. The phenomenon originates from the full oxidation of the reduced Mo species to Mo^{6+} induced by Oso. In parallel with other reactions involving oxygen, this confirms that the real active and selective state of molybdenum-containing oxides is that slightly reduced possessing Mo^{5+}. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Bismuth molybdate catalysts; Oxygen assisted dehydration; 2-butanol; Spillover oxygen; Remote control mechanism

1. Introduction

This paper is an attempt to shed light on the catalytic properties of the various bismuth molybdates (α-$Bi_2Mo_3O_{12}$, β-$Bi_2Mo_2O_9$, γ-Bi_2MoO_6) in reactions involving oxygen. These phases are modestly active and selective compared to industrial multi-element, multi-phase catalysts containing Bi and Mo. Nevertheless, each of them individually has been the subject of numerous investigations. Actually, they are rarely pure and often contain small amounts (ca. 2%) of other phases. Reports are quite scattered concerning their Bi/Mo surface and bulk ratios. In addition, results concerning their activity are contradictory. As an example, the following is reported about the performances of the Bi molybdate phases for the selective oxidation (Ox) of propene (C_3=) to acrolein:

Refs. [1,2]	$\beta>(\alpha=\gamma)$
Ref. [3]	$(\beta=\alpha)>\gamma$
Ref. [4]	$\gamma>\beta>\alpha$

Similarly, in the oxidative dehydrogenation (ODH) of butene (C_4=) to butadiene, reports for conversion are:

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Ref. [5]	γ>β>α
Ref. [6]	β>α>γ

These lists are far from exhaustive.

Reports concerning multiphasic systems containing Bi molybdates confirm that the matter is mainly the cooperative effects in which they are involved. Some examples are shown in Table 1.

New approaches are therefore in strong demand for clarifying the roles of bismuth molybdates in the performances of selective oxidation catalysts. To do so, the phases must remain unchanged in the preparation procedure and in the catalytic reaction, and this must be verified. In order to minimize surface contamination phenomena, formation of new phases, aggregation or possible segregations, we used mechanical mixtures of the bismuth molybdate phases prepared separately.

Dehydration reactions on mixtures of oxides are activated by the presence of molecular oxygen. This can appear as a surprising effect as oxygen does not react with the reactants. However, we have shown a very strong parallelism between these dehydrations, Ox and ODH reactions. The catalysts are identical and the influence of the O_2 pressure is similar [11]. In addition, previous investigations showed that MoO_3 loses dehydration activity in the absence of oxygen [12]. The phenomenon is interpreted as the reduction of Mo at the surface, which is shown to happen to some extent even in the presence of O_2 [13]. The reduction is a consequence of the total combustion of the alcohol simultaneous to the dehydration. The corresponding loss of O atoms from the surface of the catalysts induces a loss of Brönsted acid sites, which most likely consist in superficial O atoms having fixed H atoms. This clarified the necessity to have oxygen in the feed to maintain the dehydration activity of oxides and justifies the use of the words “oxygen-assisted dehydration” for this system.

The advantage of oxygen-aided dehydration as a tool for investigation is that the role of oxygen in the system is to modify catalytic sites and tune the state of the catalytic surface. It is thus possible to question the role of spillover oxygen and remote control mechanism in this effect. We therefore selected the oxygen-aided dehydration of 2-butanol as test reaction. The reaction takes place at low temperature, thus minimizing the danger of parasitic reactions of the reactants. We evaluated the positions of the three Bi molybdates on the spillover oxygen donor–acceptor scale. To do so, we investigated the performances of mixtures of each Bi molybdate with MoO_3 (a typical spillover oxygen acceptor) and with α-Sb_2O_4 (a typical spillover oxygen donor). Additionally, three mixtures combining the molybdates two-by-two were also tested.

The objective of this study is to present new results which could be useful to elucidate the controversy in the literature mentioned above and to understand the origin of the high performances of multiphasic catalysts containing bismuth molybdates. The aim of our work is to show that in bismuth molybdate catalysts, a catalytic cooperation via a spillover effect offers a true understanding of their catalytic activity in the presence of oxygen.

2. Experimental

2.1. Catalyst preparation

$Bi_2Mo_3O_{12}$, $Bi_2Mo_2O_9$ and Bi_2MoO_6 were prepared by the citrate method from $Bi(NO_3)_3\cdot5H_2O$, $(NH_4)_6MoO_7O_{24}\cdot7H_2O$ and $C_6H_8O_7\cdot H_2O$. Aqueous solutions of Bi^{3+} and Mo^{6+} (Bi/Mo molar atomic ratio equal to 2/3, 1/1 and 2/1, respectively) are added to an aqueous solution of citric acid in equivalent amount. The water was evaporated under vacuum in a revolving flask at 30°C until a viscous solution was obtained. This solution was dried at 80°C under

Table 1
Explanations given in the literature for the cooperative effects between Bi molybdates

Authors	Type of cooperation	Explanation
Matsuura et al. [6]	α+γ in n-C_4=ODH	Formation of a phase similar to β
Carson et al. [7]	α+β in n-C_3=Ox	Deposition of α or γ
El Jamal et al. [8,9]	α+γ in n-C_3=Ox	Elimination of Bi-rich layer on the reaction of this Bi with α
Weng et al. [10]	α+various oxides in n-C_4=Ox	Action of spillover oxygen

vacuum for 16 h in order to obtain a spongy precursor which was crushed, decomposed at 300°C for 16 h and calcined at 470°C for 18 h. Pure α-Sb_2O_4 and MoO_3 were obtained by calcination of Sb_2O_3 and $(NH_4)_6MoO_7O_{24}\cdot 7H_2O$, respectively, in air at 500°C for 20 h. All reactants were pure grade.

The mechanical mixtures contained equal mass flocations of: (i) two bismuth molybdates, (ii) one bismuth molybdate and α-Sb_2O_4 or MoO_3, and (iii) α-Sb_2O_4 and MoO_3. The starting powders were interdispersed in *n*-pentane and then dried at 110°C. The mixtures were not further calcined at high temperatures.

2.2. Catalytic tests

The catalytic measurements were performed in a conventional fixed-bed reactor in the up-flow mode at atmospheric pressure with 1 g of catalyst pellets sieved between 0.315 and 0.500 mm. The feed (34 ml/min) contains a partial pressure of 176 mm Hg of 2-butanol (BUT) in air corresponding to a volume ratio BUT/oxygen of 1.5/1. Two reaction temperatures were chosen: 220 and 250°C. Analysis of the products was done using on-line gas chromatography. Catalytic performances were expressed as conversion of 2-butanol (%*C*), selectivity (%*S*), and yield (%*Y*) to butene. One did not try to differentiate the different butene isomers.

2.3. Catalyst characterisation

All catalysts were characterized before and after the catalytic test using the BET technique, XRD, Raman spectroscopy and XPS. BET surface areas were measured using a Micromeritics ASAP 2000 instrument by adsorption of krypton at −196°C on 200 mg samples previously degassed at 150°C for 2 h at a pressure of 0.001 mm Hg. X-ray diffraction patterns were obtained with a high resolution X-ray diffractometer Kristalloflex Siemens D5000 using Cu Kα radiation (λ=1.5418 Å), scanning the 2θ range between 5° and 70° at a rate of 0.25°/min.

Raman spectra were recorded with a Perkin-Elmer Spectrum 2000 in the range $700-1000\ \text{cm}^{-1}$. The samples were irradiated by a Nd/YAG laser (λ=1064 nm) with a power of 200 mW. The spectral resolution was $4\ \text{cm}^{-1}$ and the number of scans was 20.

For X-ray photoelectron spectroscopy, SSX-100 Model 206 SSI spectrometer with monochromatized Al Kα radiation (1486.6 eV) was used. Vacuum in the analysis chamber was 5×10^{-9} Torr. Charge neutralisation was achieved using an electron flood-gun adjusted at 6 eV and placing a Ni grid 3.0 mm above the sample. The recorded peaks were C1s (284.8 eV), $Bi4f_{7/2}$ (164.7 eV), $Mo3d_{3/2}$ (235.6 eV), O1s (530.5 eV) and $Sb3d_{5/2}$ (530.4 eV) [12].

3. Results

3.1. Pure bismuth molybdates and single oxides

The α-Sb_2O_4 phase is nearly inactive. In the other cases, butenes were the only selective products obtained except for α-$Bi_2Mo_3O_{12}$ and MoO_3, which also produced traces of methylethylketone. The α phase is more active and selective than β and γ phases (Table 2).

XRD and Raman patterns correspond to the respective α, β and γ phases. The BET surface areas and these patterns remained unchanged after reaction. Concerning the XPS signal for Mo, all spectra presented a shoulder for the $Mo3d_{3/2}$ peak at about 231.0 eV, which is attributed to Mo^{5+}. A typical profile of the $Mo3d_{3/2}$ band with a Mo^{5+} contribution is presented in Fig. 1a. XPS analysis did neither detect any modification in the atomic ratio nor Mo oxidation state nor the occurrence of any deposition of carbon at the surface after the reaction.

3.2. Mechanical mixtures of two bismuth molybdates

Conversions of 2-butanol, yields and selectivities to butenes (Table 3) obtained on the mixtures were

Table 2
Surface area and catalytic activity at 220°C of pure oxides in the oxygen-assisted dehydration of 2-butanol

Oxides	S_{BET} (m^2/g)	%*C* (2-butanol)	%*Y* (butenes)	%*S* (butenes)
α-$Bi_2Mo_3O_{12}$	1.30	35.3	12.3	34.8
β-$Bi_2Mo_2O_9$	1.40	14.5	3.7	25.7
γ-Bi_2MoO_6	1.60	11.6	3.4	29.0
MoO_3	3.33	86.9	33.6	38.0
Sb_2O_4	1.49	0.6	0	0

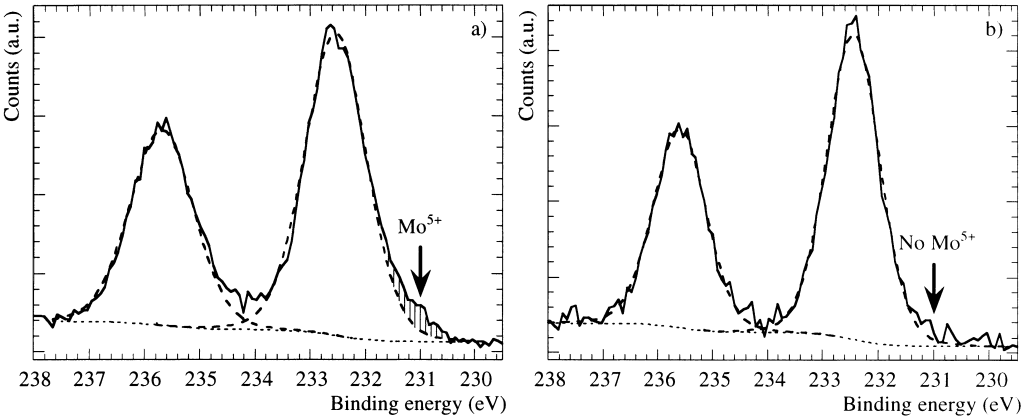

Fig. 1. XPS Mo3d band for the mechanical mixture of Bi_2MoO_6 and α-Sb_2O_4: (a) before catalytic test, and (b) after catalytic test. The plain line represents the raw spectrum; the dotted line represents the baseline; the dashed line represents the Mo^{6+} contribution. In (a), the dashed area is not covered by the Mo^{6+} contribution, indicating the presence of Mo^{5+} species. In (b), the Mo^{6+} contribution fits perfectly the raw spectrum, suggesting the absence of Mo^{5+} species.

always higher than those theoretically calculated on the basis of the performances of the pure phases, indicating the existence of a synergy between the different molybdate phases. BET surface areas, XRD and Raman spectra and XPS spectra (including the shoulder at 231.0 eV for the $Mo3d_{3/2}$ band) were similar before and after the catalytic test. The XPS analysis did neither detect any atomic ratio nor Mo oxidation state modification nor carbon deposition. Under the conditions used in this work, no change of the three molybdate phases can be detected after the reaction. Therefore, the observed catalytic synergy cannot originate from aggregation or segregation effects from the formation of a new oxide phase or mutual contamination. As suggested in a previous investigation on the oxidation of isobutene to methacrolein at higher temperature (400–450°C) [11,14], a plausible explanation of the synergy rests on the existence of a cooperation between separate molybdate phases, probably via spillover oxygen.

3.3. *Mechanical mixtures of bismuth molybdates and MoO_3*

A significant synergy in the conversion of 2-butanol and the yield to butenes was observed on the mixtures (Table 4). However, selectivity corresponds to the value expected if both components behaved independently. BET, XRD, Raman and XPS techniques did not detect any modification of the catalysts after the reaction.

It is striking that compared to the mixture of MoO_3 with α-Sb_2O_4, the intensity of the synergies are al-

Table 3
Catalytic performances at 220°C of the mechanical mixtures of bismuth molybdates[a]

Mechanical mixtures	%*C* (2-butanol)	%*Y* (butenes)	%*S* (butenes)
α-$Bi_2Mo_3O_{12}$–β-$Bi_2Mo_2O_9$	35.0 (24.9)	12.2 (8.0)	34.9 (32.1)
α-$Bi_2Mo_3O_{12}$–γ-Bi_2MoO_6	32.4 (23.4)	10.7 (8.0)	34.9 (34.1)
β-$Bi_2Mo_2O_9$–γ-Bi_2MoO_6	15.4 (13.0)	4.7 (3.5)	30.8 (27.1)

[a] Values in parentheses are those theoretically calculated from the results obtained with the individual catalysts admitting the approximation of zero order kinetics.

Table 4
Catalytic performances at 220°C of the mechanical mixtures of the bismuth molybdates and MoO_3[a]

Mechanical mixtures	%*C* (2-butanol)	%*Y* (butenes)	%*S* (butenes)
α-$Bi_2Mo_3O_{12}$–MoO_3	73.7 (61.1)	27.5 (22.9)	37.4 (37.5)
β-$Bi_2Mo_2O_9$–MoO_3	86.0 (50.7)	32.1 (18.7)	37.3 (36.8)
γ-Bi_2MoO_6–MoO_3	81.8 (49.2)	30.5 (18.5)	37.5 (37.5)

[a] Values in parentheses are those theoretically calculated from the results obtained with the individual catalysts admitting the approximation of zero order kinetics.

Table 5
Catalytic performances of the bismuth molybdates and α-Sb_2O_4 mechanical mixtures[a]

Mechanical mixtures	%*C* (2-butanol)	%*Y* (butenes)	%*S* (butenes)
α-$Bi_2Mo_3O_{12}$–α-Sb_2O_4	19.5 (48.0)	6.7 (17.1)	34.3 (35.7)
β-$Bi_2Mo_2O_9$–α-Sb_2O_4	3.2 (25.9)	0.5 (8.4)	16.7 (32.5)
γ-Bi_2MoO_6–α-Sb_2O_4	2.9 (23.6)	0.2 (7.8)	5.7 (33.0)
MoO_3–α-Sb_2O_4	73.4 (50.1)	27.5 (19.5)	37.5 (37.9)

[a] Values in parentheses are those theoretically calculated from the results obtained with the individual catalysts admitting the approximation of zero order kinetics.

most identical for the mixtures of MoO_3 and Bi Molybdates (see last row of Table 5). The synergetic effect exerted by the latter in selective oxidations and the oxygen-assisted dehydration of formamides [14] has been shown to be due to the spillover oxygen species, Oso, that it produces. The bismuth molybdates thus behave also as Oso donors with respect to MoO_3.

3.4. Mixtures of bismuth molybdates and α-Sb_2O_4

Surprisingly, when mixing α-Sb_2O_4 with the various molybdates, the catalytic activity, yield to butene and selectivity decreased dramatically (Table 5). As for the other mixtures, specific surface areas, XRD and Raman patterns were unchanged before and after the reaction, which suggests that the loss of activity should be interpreted by some interaction between separate phases leading to inhibition. But XPS analysis showed a very different behaviour when considering the $Mo3d_{3/2}$ peak (Fig. 1).

While in all other cases (mixtures of two bismuth molybdates and mixtures of one bismuth molybdate with MoO_3), a significant part of the Mo in the bismuth molybdate phases remained stabilized as Mo^{5+} species (shoulder at 231 eV) even after the catalytic reaction, the Mo^{5+} species present before reaction in the mixture with α-Sb_2O_4 disappeared totally after the test. In the case of the mixtures with α-Sb_2O_4, Mo^{5+} got completely oxidized to Mo^{6+}. Fig. 1 shows the disappearance of the Mo^{5+} species during the reaction in the case of the mixture of Bi_2MoO_6 with α-Sb_2O_4 but the phenomenon happened for all mixtures of one bismuth molybdate with α-Sb_2O_4. These results show that bismuth molybdates behave as acceptors of oxygen spillover with respect to α-Sb_2O_4.

4. Discussion

No change of any of the α, β or γ-Bi molybdates during the catalytic reaction can be observed. Nevertheless, synergetic effects occurred. In the frame of the remote control mechanism concept, we have shown that all the oxides involved in Ox, ODH or oxygen-assisted dehydration are located at intermediate places in a spillover oxygen donor–acceptor scale [11]. Bismuth molybdates exhibit a dual behaviour but with different donor/acceptor balances. This accounts for the synergetic effects in mixtures of Bi molybdates together and in mixtures of Bi molybdates and MoO_3 (Tables 3 and 4), while these results confirm that the bismuth molybdates behave as donor of spillover oxygen with respect to MoO_3 (a typical acceptor). If the synergy in the conversion is considered, β and γ phases are stronger donors. Selectivities remain constant and are the same in all cases.

The situation for mixtures of Bi molybdates with α-Sb_2O_4 is less clear because conversions are decreased as well as selectivity for β and γ. The interesting result concerns the effect induced by α-Sb_2O_4, which is considered as an Oso donor much stronger than the bismuth molybdates themselves [11], when it is mixed with the Bi molybdates. This result may clarify the situation. The Oso donor property of α-Sb_2O_4 in the oxygen-assisted dehydration of 2-butanol at low temperature has already been proven. In a long catalytic test of 12 h, it was shown that pure MoO_3 surface got deeply reduced with a corresponding progressive transformation to MoO_2. The latter led to the deactivation of the catalyst. On the contrary, when MoO_3 was used in physical mixture with α-Sb_2O_4, its surface got stabilized to a chemical state which was just slightly reduced without any lattice destruction. The effect was attributed to the action of spillover oxygen produced by α-Sb_2O_4 on the surface of MoO_3. By maintaining MoO_3 in a more active suboxide structure, the presence of α-Sb_2O_4 thus led to a "synergetic" increase of the 2-butanol conversion and selectivity to butene [13,15], but the effect of α-Sb_2O_4 in the case of the Bi molybdates was completely opposite. α-Sb_2O_4 induced a strong decrease of the activity and selectivity of the β and γ-Bi molybdates, and to a lesser extent, of the α phase. In the absence of structural modification of the molybdates, we should admit that this effect is also due to an action of Oso on these catalysts. In parallel with the catalytic results, we found that another effect of α-Sb_2O_4 was to induce oxidation of the reduced Mo species of the Bi molybdates to fully oxidized Mo^{6+}. The phenomenon particularly concerned the γ phase which suffered the most important loss of activity. Such an oxidation was never observed for the other catalysts, where Bi molybdates exhibited their usual reactivity, or better, developed synergetic effects. Therefore, our hypothesis is that the loss of activity is intimately related to the full oxidation of the reduced Mo species. The molybdates are acceptors, but *too strong* acceptors, in the sense that they deactivate by forming stoichiometric or near-stoichiometric oxides.

In the case of MoO_3, not only in the oxygen-assisted dehydration of 2-butanol [15], but also in the selective oxidation of isobutene to methacrolein [13,16–18], the best catalytic performances were indeed obtained when the surface of the oxide was maintained in a slightly reduced state as it is often commented in literature. Bi molybdates have a structure which can undergo changes very similar to those of MoO_3. Our assumption is thus that the compounds should also behave similarly from the catalytic point of view. By eliminating the few reduced Mo species at the molybdate surface, α-Sb_2O_4 led to the destruction of the most active and selective state of the catalyst. The resulting effect is the decrease of performances that we have observed.

5. Conclusion

Under the assumption of the remote control mechanism, the three Bi molybdates, α, β and γ, have been shown to develop a dual role. They influence the reactivity of the catalytic system as typical oxygen spillover donor when reacted in the presence of a typical acceptor (like MoO_3), but at the opposite they act as oxygen spillover acceptor (they have their surface oxidized) when in the presence of a typical donor (like α-Sb_2O_4). This duality is the origin of the synergetic effects and the mutual increase of performances they exhibited when mixed together. Remembering that the Bi molybdates are rarely synthesized completely pure, this likely elucidates the reason of the controversial performances previously reported by various authors in the literature.

Another result is that the Bi molybdates exhibit their highest performances when they are maintained in a slightly reduced state. We previously drew an identical conclusion concerning the reactivity of MoO_3. This result is important since it shows that our previous conclusions concerning the reactivity of MoO_3 in selective oxidation, oxidative dehydrogenation and oxygen-assisted dehydrations identically apply for other compounds with similar structural properties. The present investigation concerned Bi molybdates, but one presumes that other catalysts often used in industrial processes also obey the same rules.

In addition, beyond that aspect, our results open other perspectives. Oxygen-assisted dehydration reactions of 2-butanol like in this work or of *N*-ethyl-formamide to propionitrile [14] are due to Brönsted acid sites. We previously showed that such Brönsted sites could be created under the action of spillover oxygen. In the present work, it is shown that spillover oxygen can also influence the reactivity of oxides in dehydration reactions by dictating their oxidation state and controlling their suboxidic character. Our results thus confirm that there is an intimate link between the presence of acid sites at the surface of oxides and their suboxide structure. This point has to be investigated further to fully reveal its potential importance for the understanding and improvement of the selective oxidation processes.

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