

Catalytic Synergy between MoO₃ and BiPO₄ in *N*-Ethyl Formamide Dehydration

II. Characterization of Mixtures of MoO₃ and BiPO₄

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This paper concerns the physicochemical characterization of mixtures of BiPO₄ and MoO₃ powders whose catalytic activity in the dehydration of *N*-ethyl formamide has been reported previously. The aim of the work was to investigate whether the existence of any mixed BiPmo oxide species, due to a contamination of the surface of one phase by elements coming from the other phase, could explain the synergy. Analytical Electron Microscopy (AEM) detects a contamination of BiPO₄ by MoO₃ only when the mixture is prepared from suspensions of BiPO₄ and MoO₃ in water. Electron Spectroscopy for Chemical Analysis-X-Ray Photoelectron Spectroscopy (ESCA-XPS) results cannot give any valuable information with respect to contamination, due to the relatively important thickness of the surface layer analyzed. Ion Scattering Spectroscopy shows a contamination in the same case as AEM. The MoO₃-contaminated layer is easily removed by ion sputtering. We conclude that, except for the fresh mixture prepared with water, no surface contamination of one phase by elements of the other phase can be detected in fresh catalysts or in catalysts having worked in the reacting mixture of *N*-ethyl formamide and oxygen at moderate temperatures. © 1986 Academic Press, Inc.

INTRODUCTION

In the preceding article (1), we presented results concerning the activity of catalysts obtained by mixing MoO₃ powders with BiPO₄ powders. We attributed the synergy between these two phases to a *remote control mechanism*. However, we indicated that synergy, in principle, might be due to phenomena distinct from the remote control mechanism. Classical bifunctionality had to be ruled out. There still remained to take into account the possibility of promotion of activity of one phase by minute amounts of elements of the other. The present article concerns the physicochemical characterization of our catalysts with, as a principal objective, the detection of such a contamination, due either to the preparation procedure or to catalytic work.

Three techniques were used. Analytical electron microscopy (AEM) can give us an

information about the composition of each particle (of each phase) as a whole, namely taking together bulk and surface. ESCA-XPS informs about the composition of the outmost surface layers but cannot give separate information for each of the single phases. Ion Scattering Spectroscopy (ISS) analyzes successively the surface layers, starting from the topmost one. But it also gives the average values of the signals coming from both types of particles. But, in principle, the study of the changes in the signals ratio with sputtering time can give valuable information on the presence, on one phase, of a contaminating layer constituted of one or several elements of the other phase.

In catalytic experiments and in the reduction and reoxidation experiments, mechanical mixtures of MoO₃ and BiPO₄ of 8 m² · g⁻¹ each ("standard" samples) gave the most conspicuous results (1). The maxima

TABLE I
Characteristics of Pure Powders and Mixed Catalysts

Single phases			
Catalyst	S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$)	Phases (X ray)	
BiPO ₄ "standard"	8.2	Hexagonal	
MoO ₃ "standard"	7.9	Orthorhombic	
Mixed catalysts			
Method of mixing	r	S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$)	S_{av}^a ($\text{m}^2 \cdot \text{g}^{-1}$)
Cogrinding	0.500	8.1	8.10
Dispersion-freeze-drying in H ₂ O	0.500	7.8	8.10
Dispersion-freeze-drying in <i>n</i> -pentane	0.500	8.1	8.10

^a S_{av} is the properly averaged value from values of S_{BET} for single phases taking into account the weight fractions, s and $1 - s$, of the phases in the mixtures: $S_{\text{av}} = s S_{\text{BiPO}_4} + (1 - s)S_{\text{MoO}_3}$.

of catalytic activity and reducibility appeared for MoO₃/BiPO₄ = 1/1 (1, 2). We therefore investigated samples with this composition. We compared with samples prepared by coprecipitation (3–5).

EXPERIMENTAL

Catalyst Preparation

We indicated, in the previous article (1), the reagents used and the detailed preparation of the MoO₃ and BiPO₄ powders. It suffices to recall that MoO₃ and BiPO₄ powders of 8 m² · g⁻¹ each were prepared separately and that catalysts were made by mixing these powders, either by simply grinding them gently together, or by dispersing them in water and freeze-drying the suspension, or by dispersing them in *n*-pentane and freeze-drying the suspension.

The second and third methods were hoped to minimize physical damage of the individual crystallites. We contemplated the possibility that the second method might bring about some contamination of BiPO₄ by MoO₃, as a consequence of the slight solubility of MoO₃ in water. The first

and, particularly, the third method should, on the contrary, minimize such a contamination.

The characteristics (1, 2) of the pure powders and of the mixed catalysts are recalled in Table 1. The composition of the mixed catalysts is indicated by the molar ratio $r = \text{MoO}_3/(\text{MoO}_3 + \text{BiPO}_4)$. The surface areas of the physical mixtures always correspond to the sum of the contribution of each individual phase (S_{av} , see Table 1). Single-phase MoO₃ showed the lines characteristic of the orthorhombic phase, while BiPO₄ was hexagonal. The mixing procedure did not modify the crystalline phases.

Catalytic Activity

It suffices to recall (1) that catalytic activity is quite sensitive to the presence of oxygen. We investigated principally the fresh catalysts. In addition, some samples were contacted with the reacting mixture in the flow apparatus used for catalytic tests, as described in (1), and these samples were subjected to physicochemical investigation after exposure to air at room temperature.

Analytical Electron Microscopy and other Methods of Microscopy (EM)

AEM examinations were made with a Jeol Temscan 100 CX electron microscope equipped with a Kevex 5100 C energy dispersive spectrometer. Samples were ground, dispersed in ethanol, and deposited on a carbon film supported on a copper grid.

Samples were examined in the scanning transmission (STEM) and in the secondary electrons scanning (SEM) mode. The composition of the different phases was determined by means of the energy dispersive spectrometer coupled to the microscope. In principle, it is possible, with this instrument, to analyze the bulk composition of each type of particles (MoO_3 or BiPO_4) in order to detect contamination. The lower limit of detection corresponds to a content of about 1% of the contaminating phase on the other phase.

ESCA-XPS

ESCA-XPS measurements were carried out in a Vacuum Generators ESCA-3 equipment; the exciting radiation was $\text{AlK}\alpha$ (1486.6 eV). The recording sequence was maintained the same for all the samples in order to avoid spurious effects due to the progressive contamination of the sample in the course of the analysis. Total accumulation time was about 5 h. The C 1s, O 1s, P 2p, Mo 3d_{5/2} and Mo 3d_{7/2}, Bi 4f_{5/2}, C 1s lines were swept successively. The C 1s line of adventitious carbon was used as reference (BE = 285 eV). Concentrations were calculated from XPS intensities by using "atomic sensitivity factors" given by Wagner *et al.* (6).

Ion Scattering Spectroscopy (ISS)

The ISS measurements were performed with a Kratos instrument (Wg 541 Type 515). The core of the spectrometer consists of a cylindrical mirror analyzer (CMA) with an energy resolution $\Delta E/E = 0.03$ and a predominant scattering angle of 138°. A

coaxial electron bombardment type ion gun is integrated within the CMA. This system is mounted vertically in a UHV chamber in which the base pressure is about 5×10^{-9} Torr. During analysis, the noble gas to be ionized is introduced into the chamber to a pressure varying from 2×10^{-7} to 2×10^{-6} Torr. A SIMS system (Riber Q 156) is also present in the chamber, and combined ISS-SIMS measurements can be performed simultaneously on the same impact area.

The catalyst powder was compressed in small cups which were supported horizontally in the chamber and were bombarded at normal incidence. He^+ ions were used for ISS analysis. The beam energy E_0 was 1.5 keV and the beam current was 10 nA, with a spot size of 350 μm . A positive charge accumulates on the surface during bombardment by He^+ ions since these catalysts are electrical insulators. A hot W filament was used to provide a flow of thermal electrons to compensate this charge.

During the analysis, the ion beam was rastered over a square area of $(1 \times 1) \text{mm}^2$ and an electronic gate allowed the analyzer to accept only scattered ions coming from the central part. This procedure has shown to improve the charge compensation and is known to reduce the crater effects while depth profiling with ion beam (7).

The acquisition and the accumulation of the spectra were done with a fully programmable multichannel analyser (Lecroy MCA Model 3500). A spectrum was taken in 9 s and automatic sequences of analysis and sputter etching were performed. The ISS energy spectra have been converted into mass spectra by means of the single binary elastic collision model:

$$\frac{E_i}{E_0} = \left[\frac{\cos \theta + (\gamma^2 - \sin^2 \theta)^{1/2}}{(1 + \gamma)} \right]^2, \quad (1)$$

where E_i is the measured scattered ion energy of initial energy E_0 , θ is the scattering angle, and $\gamma = M_i/M_0$; M_i is the unknown mass of the surface target atom and M_0 is the projectile ion mass.

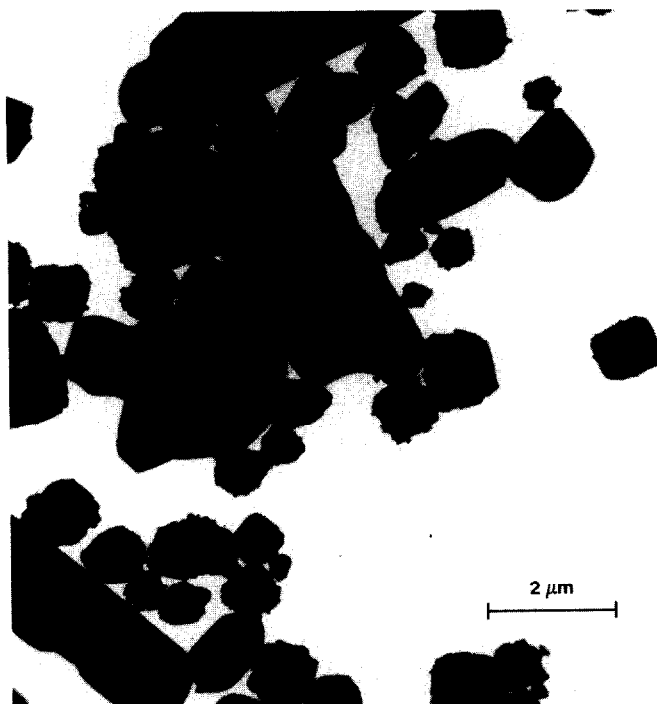


FIG. 1. STEM picture of MoO_3 - BiPO_4 (1:1) prepared by cogrinding.

RESULTS

AEM and other Methods of Microscopy

Samples of MoO_3 - BiPO_4 (1:1 molar) prepared either by cogrinding or by dispersion-freeze-drying in water showed very similar morphologies, so that only EM pictures for the mixture prepared by cogrinding are given.

Figure 1 shows a STEM picture of this sample. The bigger and smoother particles are composed of pure MoO_3 as indicated by their electron probe microanalysis spectra (Fig. 2 a). Spectra of the other type of particles (Fig. 2 b) correspond to pure BiPO_4 .

Figure 3 is a SEM view which indicates the different surface morphologies of both types of particles. MoO_3 particles exhibit smooth surfaces, while BiPO_4 show highly irregular surfaces. Figure 4 is a magnification (SEM) of the region of contact between two particles of different types.

As mentioned earlier, mechanical mixtures obtained by dispersion-freeze-drying

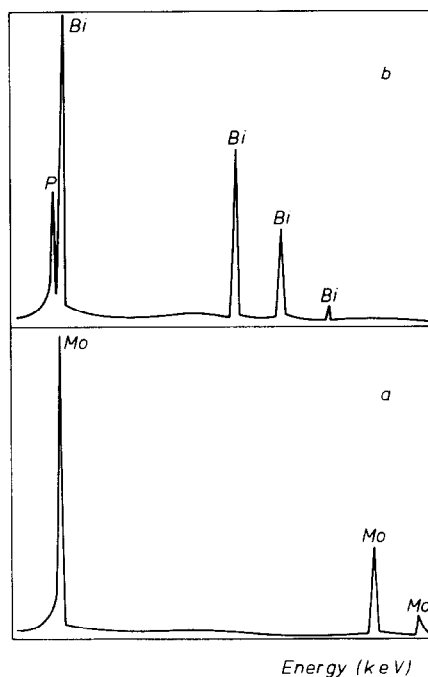


FIG. 2. EPMA spectra of MoO_3 - BiPO_4 (1:1) prepared by cogrinding. (a) MoO_3 particle; (b) BiPO_4 particle.

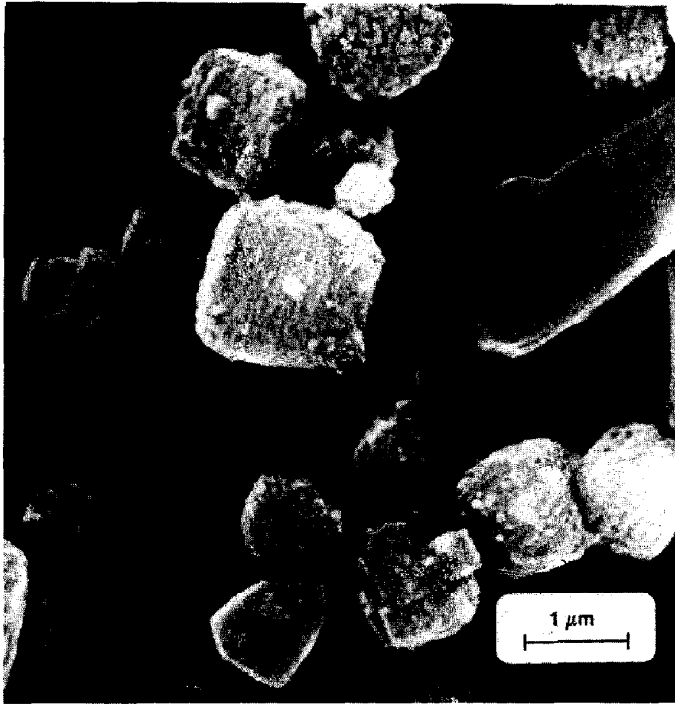


FIG. 3. SEM picture of MoO₃-BiPO₄ (1 : 1) prepared by cogrinding.

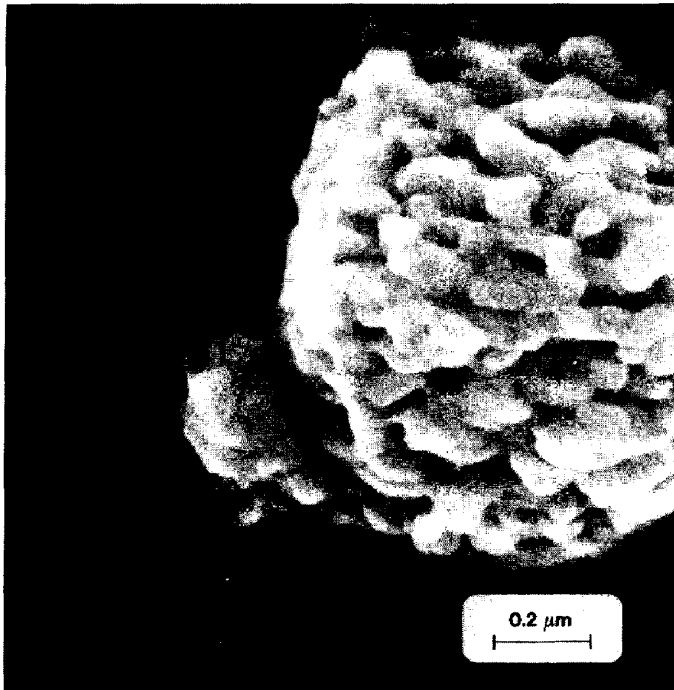


FIG. 4. SEM magnification of the contact region between two particles of different types, from Fig. 3.

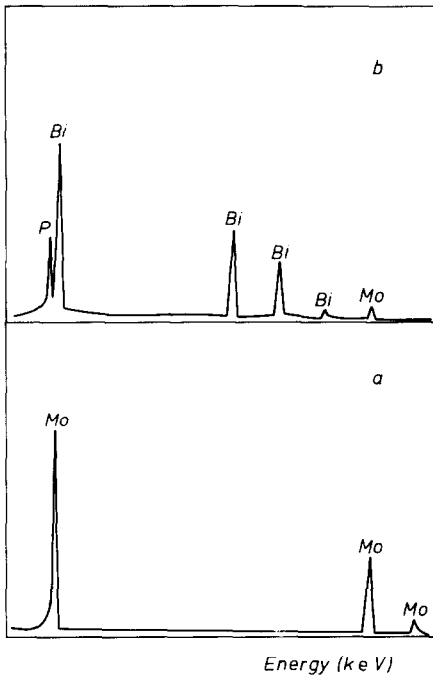


FIG. 5. EPMA spectra of $\text{MoO}_3\text{-BiPO}_4$ (1:1) prepared by dispersion-freeze-drying in H_2O . (a) MoO_3 particle; (b) BiPO_4 particle.

in water show morphologies similar to those of mixtures prepared by cogrinding. But there is an interesting difference in the electron probe microanalysis spectra: particles of the BiPO_4 show, in this case, some contamination by Mo (Fig. 5b), while particles of MoO_3 are pure (Fig. 5a). We verified the presence of that contamination by taking the spectra for a great number of BiPO_4 particles.

A rather different picture is observed for samples of $\text{MoO}_3\text{-BiPO}_4$ (1:1) prepared by dispersion-freeze-drying in *n*-pentane. Figure 6 shows the appearance of two very different types of particles: one type is composed of pure MoO_3 and is similar in shape to MoO_3 particles present in the mechanical mixtures prepared by the other two methods. The other type of particles correspond to pure BiPO_4 ; they appear, in the present sample, mainly as needle-shaped, and are much smaller than the MoO_3 particles. Figure 7 shows a SEM picture of this sample. Particles of BiPO_4 are clearly irregular and wrinkled. Particles of



FIG. 6. STEM picture of $\text{MoO}_3\text{-BiPO}_4$ (1:1) prepared by dispersion-freeze-drying in *n*-pentane.



FIG. 7. SEM picture of $\text{MoO}_3\text{-BiPO}_4$ (1 : 1) prepared in dispersion-freeze-drying in *n*-pentane.

MoO_3 are regular in shape, smooth, and seem to have a layer structure.

Some samples of the mechanical mixture (1 : 1) obtained by dispersion-freeze-drying in *n*-pentane were examined after exposure to catalytic reaction conditions for 1 h at 275°C, either in the presence of O_2 at $\text{O}_2/\text{formamide} = 4$ (molar) ("standard" conditions) or in total absence of oxygen. That was done in order to detect any modification in the morphology or in the phase composition in the course of catalytic work in very different conditions. Samples that have worked either in the absence or in the presence of oxygen show morphologies closely similar to that of the fresh catalyst. Contamination of one phase by the other was never detected, whichever the sample examined.

ESCA-XPS

Values of binding energies (BE) for O 1s, P 2p, Bi 4f_{7/2}, Bi 4f_{5/2}, and Mo 3d were practically constant in the $\text{MoO}_3\text{-BiPO}_4$ cata-

lysts whichever the mixing method employed. For the mixture (1 : 1) prepared by dispersion-freeze-drying in water it was observed that the BE values for Bi 4f_{7/2}, Bi 4f_{5/2}, and Mo 3d diminished regularly when the conditions of the catalytic reaction became more and more severe (decreasing O_2 concentration and increasing temperature).

Table 2 presents the results concerning selected ESCA-XPS analyses of the (1 : 1) mechanical mixtures. The surfaces of samples prepared by cogrinding and by dispersion-freeze-drying in water exhibit a similar composition for the elements Bi, P, and Mo, this last element representing half of the exposed surface cations. On the contrary, the mixture prepared by dispersion-freeze-drying in *n*-pentane has a surface richer in Bi and P than in Mo. As an indication of the reproducibility of this type of samples preparation and analysis, results are given for two different samples (separately dispersed and freeze-dried in *n*-pentane).

TABLE 2
 ESCA-XPS Concentrations

Samples of MoO_3 - BiPO_4	$\frac{I_P}{\sum I_i}$	$\frac{I_{\text{Bi}}}{\sum I_i}$	$\frac{I_{\text{Mo}}}{\sum I_i}$	$\frac{I_O}{\sum I_i}$
Cogrinding ($r = 0.500$)	0.315	0.186	0.499	0.749
Dispersion-freeze-drying in water ($r = 0.500$)	0.293	0.180	0.527	0.752
Dispersion-freeze-drying in <i>n</i> -pentane ($r = 0.500$) (Sample A)	0.461	0.254	0.285	0.742
Dispersion-freeze-drying in <i>n</i> -pentane ($r = 0.500$) (Sample different from A)	0.469	0.259	0.271	0.743

Note. $\sum I_i = I_P + I_{\text{Bi}} + I_{\text{Mo}}$; $\sum I_s = I_P + I_{\text{Bi}} + I_{\text{Mo}} + I_O$.

The surface composition for samples of the mechanical mixture 1:1 varies after catalytic work. The samples exposed to the most severe conditions (less O_2) became progressively enriched in Mo and in O at their surface, especially for O_2 /formamide ratios lower than 1.

ISS

ISS spectra have been measured on different samples: the samples constituted of a mixture of MoO_3 and BiPO_4 with a molar ratio 1:1 prepared by the different methods and the pure single phases MoO_3 and BiPO_4 .

The ISS intensity increases during the bombardment until a constant value is obtained. This has been interpreted as due to the desorption of low mass impurities contaminating the surface under the ion impact

(8). Figures 8 and 9 show the stationary spectra obtained after 5 min of bombardment. The sample prepared by dispersion in water (Fig. 9b) exhibits a marked difference compared to the other spectra. In this case, the Mo contribution is greater than that of Bi. A sodium contamination is observed on the sample prepared by cogrinding (Fig. 9a). The sample prepared by dispersion in *n*-pentane shows a reduction of the O contribution of about 10% after being used in a catalytic reaction experiment (compare

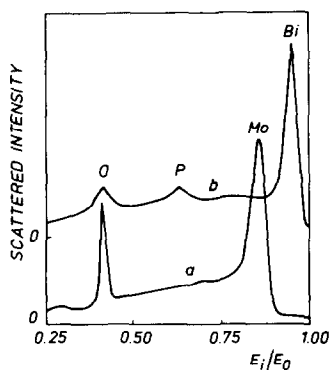


FIG. 8. He^+ (1.5 keV) ISS spectra at $\theta = 138^\circ$. (a) MoO_3 ; (b) BiPO_4 .

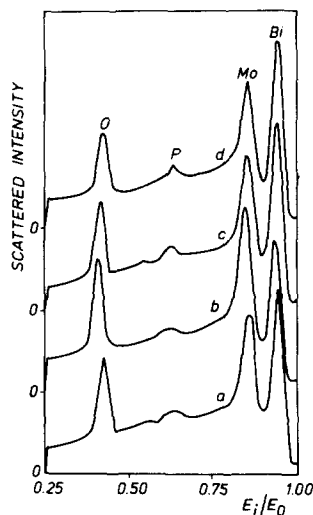


FIG. 9. He^+ (1.5 keV) ISS spectra at $\theta = 138^\circ$ of MoO_3 - BiPO_4 (1:1) prepared by different methods. (a) Cogrinding; (b) dispersion-freeze-drying in H_2O ; (c) dispersion-freeze-drying in *n*-pentane; (d) same as in (c) after catalytic work for 1 h at 275°C and O_2 /formamide = 4 (molar).

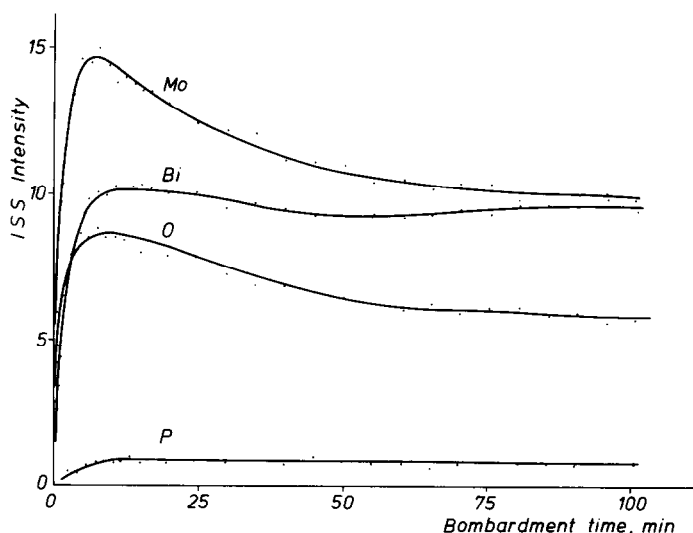


FIG. 10. Evolution of the ISS peak maxima as a function of time for the catalyst $\text{MoO}_3\text{-BiPO}_4$ (1 : 1) prepared by dispersion-freeze-drying in H_2O .

Figs. 9c and d). Once the steady state is attained, no drastic evolution of the spectra were found as a function of the bombardment time.

Since the sample prepared by dispersion in H_2O gave different results, a detailed analysis of the evolution of the ISS spectra with bombardment has been made for this sample. Figure 10 shows the variation with the sputter time of the peak maximum intensities measured above the background. After the rapid increase mentioned above, the Bi and P contributions remain nearly constant while the Mo and O contributions decrease and afterward reach a plateau.

DISCUSSION

Electron Microscopy

STEM micrographs show that samples prepared by cogrinding and by dispersion-freeze-drying in water are composed of particles of MoO_3 and BiPO_4 of similar sizes. SEM micrographs show that particles of MoO_3 present a smooth surface, while BiPO_4 particles seem to be aggregates of very small particles. Mechanical mixtures prepared by dispersion-freeze-drying in *n*-pentane possess rather different character-

istics. It seems that, under the influence of the dispersion in *n*-pentane, aggregates of BiPO_4 have been disintegrated to smaller particles. According to Table 1, this phenomenon does not modify the specific surface area with respect to that of the MoO_3 and BiPO_4 starting phases. SEM suggests that MoO_3 particles possess a layer structure. It seems likely that pores existing between the parallel plates can account for a specific surface area of the same order as that of BiPO_4 .

Electron probe microanalysis spectra for the three samples show that those prepared by cogrinding and by dispersion-freeze-drying in *n*-pentane are composed of MoO_3 and BiPO_4 separate phases, pure or, at least, containing less than a 1% concentration of the elements of the other phase. By contrast, in the sample prepared by dispersion-freeze-drying in water, a detectable amount of Mo is present in the particles of BiPO_4 . The level of contamination, however, remains very low. Quantitative evaluation of this contamination is difficult. Let us suppose it is of the order of 1% MoO_3 . This would correspond to about 0.87 monolayers of MoO_3 , considering that

one molecule of MoO₃ in a monolayer structure covers 0.17 nm² (9).

The existence of this contamination in samples freeze-dried in water is easily explained. When MoO₃ and BiPO₄ are both mixed in water, only a minute amount of BiPO₄ is dissolved (the solubility product of BiPO₄ has a mean value of 1×10^{-23} (10)); however, MoO₃ has a substantial solubility in water ($s = 0.1822$ wt% at 23°C (11)), so that a nonnegligible quantity of MoO₃ is dissolved. When the solvent is evaporated by freeze-drying, a part of this MoO₃ is deposited on the BiPO₄ phase.

The sample prepared by dispersion-freeze-drying in *n*-pentane is more active catalytically (1) than the sample prepared in water. Our results suggest that synergy for catalytic activity is not related to a contamination effect, but one must remember that in the most active sample a better degree of contact between BiPO₄ and MoO₃ is achieved thanks to the fragmentation of the BiPO₄ particles.

Samples of the mechanical mixture prepared in *n*-pentane, subjected to catalytic work at various oxygen concentrations, show morphologies closely similar to that of the fresh sample. Electron probe microanalysis spectra show that, within the sensitivity limits of the technique, the separate phases are pure. This suggests that no contamination of one phase by the other seems to appear following catalytic work.

ESCA-XPS

A shift of the binding energy in ESCA, compared to the position in the pure compound, may be expected, in our samples, either if the valency state of a species changes, or if a species is in a new environment. Experimental results indicate changes for Mo 3*d*: the binding energies diminish regularly for catalysts exposed to increasingly severe reaction conditions, indicating that the absence of oxygen provoked a progressive reduction of molybdenum, very likely starting at the surface of these oxides. A similar trend was observed for Bi

4*f*_{7/2} and Bi 4*f*_{5/2}. The conclusion is that all the observed effects are fully accounted for by reduction rather than by contamination of one phase by the other. This is in accordance with ESR results on the same catalysts (2). We could expect to detect anomalous Mo signals if Mo contamination of the BiPO₄ surface took place. Actually, the Mo(V) signals were normal so that no anomalous Mo due to contamination could be detected by ESR.

ESCA-XPS intensity results for the MoO₃-BiPO₄ mixtures prepared by different mixing methods were parallel to those of AEM. Surface compositions for the samples prepared by cogrinding and by dispersion in water were very similar; however, in the sample prepared by dispersion-freeze-drying in *n*-pentane, we observe comparatively a surface enrichment in P and Bi. In connection to AEM results, we attribute this to a change in the relative states of dispersions of MoO₃ and BiPO₄; the aggregates of BiPO₄ particles should be disintegrated by *n*-pentane in the dispersion step.

When samples prepared by dispersion-freeze-drying in *n*-pentane were exposed to catalytic reaction conditions, and especially at high temperatures and low oxygen concentrations, a clear increase in molybdenum concentrations was observed. This would be explained, either by a redispersion of the MoO₃ phase, or by a deposition of some coke on BiPO₄, this avoiding the possibility of detecting an important fraction of this latter phase by ESCA. The fact that no increase in carbon concentration was observed in these samples with respect to the fresh one seems to rule out this last possibility.

Oxygen concentrations at the surface of our catalysts slightly increased after catalytic work, thus suggesting that no substantial reduction of the surface is observed. On the other hand, ESR spectra for catalysts treated in catalytic conditions (2) showed some reduction of Mo(VI) to Mo(V), as well as after reductions performed in hy-

drogen or under a high vacuum. This apparent contradiction between ESCA and ESR results can be due to the low sensitivity of ESCA compared to ESR. The ESR signals measured in our samples correspond to a very small concentration of Mo in the Mo^{5+} state (a mere 1 ppm Mo^{5+} can be detected under our measurement conditions). In ESCA, a measurable shift or a detectable shoulder corresponding to Mo(V) would only appear if at least 5 to 10% of Mo were reduced.

The layers analyzed by ESCA-XPS, using as we did, lines corresponding to low binding energies, are very thick, of the order of 50 Å. It is thus difficult to draw conclusions concerning the possible contamination of one phase by a fraction of a layer of a compound coming from another phase. We cannot consider that the ESCA-XPS results give us valuable information in this respect.

ISS

In order to detect a contamination layer of elements of one phase by the other phase, we need to know quantitatively the fraction of helium ions scattered from each phase.

A first approach would be to start from the general relation giving the ISS intensity corresponding to a surface species i . In the case when there is no shadowing between the surface atoms of the different species, this intensity is given as (12)

$$I_i(\theta) = I_0 n_i \frac{d\sigma_i}{d\Omega}(\theta) P_i^+ \Delta\Omega T, \quad (2)$$

where I_0 is the primary beam current; n_i is the surface density of the species i ; $d\sigma_i/d\Omega(\theta)$ is the differential scattering cross section; P_i^+ is the probability for the primary ion to stay in the ionized state after the scattering; $\Delta\Omega$ is the analyzed solid angle, and T is the transmission coefficient of the energy analyzer and the detection system.

For the CMA analyzer, T is proportional to the analyzed energy, E_i ; $d\sigma_i/d\Omega$ can be

TABLE 3

ISS Sensitivity Factors for $\theta = 138^\circ$, $E_0 = 1.5 \text{ keV}$

	$\frac{d\sigma}{d\Omega}$ ($10^{-2} \text{ \AA}^2/\text{Sr}$)	$\frac{E_i}{E_0}$	$\frac{d\sigma}{d\Omega} \cdot E_i/E_0$
O	0.074	0.410	0.030
P	0.185	0.636	0.118
Mo	0.555	0.864	0.480
Bi	0.960	0.935	0.898

calculated from the interatomic potential (Table 3 gives the values obtained with the Molière potential (13) and the Firsov screening length (14)). P_i^+ is unknown; the processes causing neutralization are not yet fully understood. This factor may differ from one species to the other and may depend on the environment of the species i (15).

Another possibility to quantify the surface composition of the samples rests on calibration experiments. One compares the spectra of the samples with those of standards obtained on the single-phase materials. For this purpose, ISS spectra of pure MoO_3 and pure BiPO_4 were measured under the same experimental conditions (see in Figs. 8a and b). Having these spectra, we analyzed those of the samples containing both phases in the following way. The intensity scale of the MoO_3 and BiPO_4 spectra were adjusted so that, when added together, they gave a composite spectrum identical to the spectrum to be analyzed. This treatment, however, makes the assumption that P_i is not modified by the presence of the elements of the other phase, an assumption which might prove false with contaminated surfaces.

Table 4 gives the so-determined surface fraction of MoO_3 and BiPO_4 in the different samples to analyze. Except for the sample prepared by dispersion-freeze-drying in H_2O , the samples apparently show a slight surface enrichment in the BiPO_4 phase. This is normal, as the BiPO_4 particles are smaller than the MoO_3 particles.

TABLE 4
ISS Surface Composition

Samples of MoO ₃ -BiPO ₄	MoO ₃ (%)	BiPO ₄ (%)
Cogrinding	41.5	58.5
Dispersion-freeze-drying in H ₂ O	52	48
Dispersion-freeze-drying in <i>n</i> -pentane	40	60
Same after catalytic activity test (1 h, "standard" reaction conditions)	38	62

In a mechanical mixture, the external area of BiPO₄ accessible to the ion beam would be substantially larger than that of MoO₃. The opposite is found for the sample prepared in H₂O. As the morphology of samples obtained by cogrinding and by dispersion-freeze-drying in water is identical, a difference necessarily shows that some contamination of the BiPO₄ surface by MoO₃ has taken place in the latter sample.

This conclusion confirms the electron probe microanalysis results and is interpreted as the consequence of the solubility of MoO₃ in water during the codispersion of the powders before freeze-drying. During depth profiling (Fig. 10) this contamination disappears and results in accordance to the 1:1 molar fraction are obtained. One should note, however, that the interpretation of the sputter depth profile on such materials is not unambiguous due to the granular geometry of the samples and possible preferential sputtering effects (16).

CONCLUSION

The conjunction of the two results of ISS (Fig. 10 and Table 4) and of AEM allows us to conclude that a contamination of BiPO₄ by MoO₃ takes place in the sample prepared by dispersion-freeze-drying in water.

Neither AEM nor ISS gave indications of any contamination with the other samples. Results of AEM and of ISS (Table 4) suggest that no contamination takes place during catalytic work, at least at low temperatures.

On the other hand, AEM and ESCA agree to show that the increase in catalytic activity in the sample dispersed in *n*-pentane is due to an improvement in the phase contact.

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