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Catalytic Synergy between MoO_3 and $BiPO_4$ in *N*-Ethyl Formamide Dehydration

I. Catalytic Properties, Reducibility, and Reoxidizability of Mixtures of MoO_3 and $BiPO_4$

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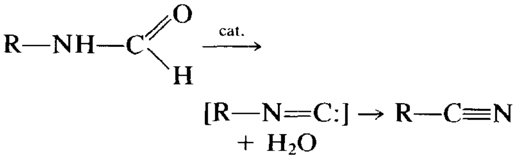
In previous publications, we reported that a catalyst composed of $BiPO_4$ and MoO_3 is active in the dehydration of formamides to nitriles. Some molecular oxygen in the feed is necessary for maintaining the catalyst active and selective. We report here results obtained with catalysts of different compositions prepared by mixing, by three different methods, separately prepared powders of $BiPO_4$ and MoO_3. The mixtures are more active than the single components. They are reduced more easily under a high vacuum or in the presence of oxygen, and they reoxidize subsequently more rapidly. A decrease of the oxygen pressure, during catalysis, depresses the magnitude of the synergetic effect, changing more the activity of the MoO_3-rich mixtures. The possible interpretations of the synergy are discussed. It is concluded that the synergy could be due to a remote control mechanism, whereby $BiPO_4$ probably produces a mobile oxygen species which, by spill-over onto MoO_3, restores catalytically active centers on this latter. The effects observed in reduction experiments are explained by a reverse spill-over. © 1986 Academic Press, Inc.

INTRODUCTION

The formation of nitriles from formamides can be classified as a homologation reaction, i.e., a reaction bringing about an increase of the hydrocarbon chain of the organic molecule. The transformation corresponds to dehydration to isonitrile, followed by rearrangement of the latter to nitrile:



$$R{-}NH{-}C(=O)H \xrightarrow{cat.} [R{-}N{=}C:] \rightarrow R{-}C{\equiv}N + H_2O$$

This reaction takes place provided molecular oxygen is present, with a remarkably high activity and selectivity over an unexpected catalytic system (*1*, *2*) composed of mixed oxides, of Bi and P on the one hand, and Mo, W, U, or V on the other hand. Oxygen is absolutely necessary for maintaining a high selectivity and for avoiding deactivation; but oxygen is otherwise inert, namely, it does not react to any appreciable extent with either feed or products in the optimum reaction conditions.

In previous publications (*3*), it has been shown that the most active catalysts, i.e., those containing Bi, P, and Mo were not composed of a single phase (e.g., some bismuth phosphomolybdate) but rather contained essentially MoO_3 and $BiPO_4$. Two-phase catalysts were remarkably more active than the single phases. There was thus clearly a synergy between $BiPO_4$ and MoO_3 for catalytic activity.

As it has been demonstrated (*3*) that, in $BiPO_4$–MoO_3 two-phase catalysts, the number of acidic sites changed when oxygen was present, one possible explanation

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of the synergy was that the nature and/or number of catalytic sites was determined by what one of us has called a *remote control effect* (*4*), namely, that a species emitted by one phase spills-over and migrates to the surface of the other phase, where it creates catalytic centers. In the present case, this mechanism demands (i) that oxygen be transferred from one phase to the other, and (ii) that the transferred species react with the surface of the second phase to create or modify catalytic centers. Because of this inferred surface reaction, it could be expected that solid-state reactions of this second solid, starting at the surface, could also be shown to take place in proper reacting conditions. Such an effect is known in the reduction of oxides (*5–7*) where spillover hydrogen, produced, for example, by a supported hydrogenation catalyst, initiates the reduction of NiO, CuO, MoO_3, etc. Similar effects, although less frequently observed, seem to occur also with oxygen (*7*).

Another finding which deserved attention was that oxygen had such a prominent influence on a catalyst (BiPMo) which is highly active in selective catalytic oxidations and ammoxidations. One logical approach to our study was thus to investigate changes in the oxide–reduction state of our catalyst in various atmospheres, as well as the changes in the catalytic properties. As most selective oxidation catalysts work, at the steady state, in a partially reduced form, it was also logical to put some emphasis on the reduction of our catalyst.

Single-phase MoO_3 and $BiPO_4$ were synthesized separately and then various physical mixtures were prepared. If a synergy for catalyzing a chemical reaction exists between two separate phases, it is reasonable to assume that this phenomenon will depend on the nature and the number of contacts between the particles of these phases. The changes in the catalyst were thus achieved either by varying the method of mixing and interdispersion, or by changing the textural properties of each starting phase.

EXPERIMENTAL

Starting Materials

The products used as starting materials for catalysts preparation were: ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, Merck, p.a.; $Bi(NO_3)_3 \cdot 5H_2O$, Merck, cryst.; $(NH_4)_2HPO_4$, UCB, p.a.; H_3PO_4 Baker, "Baker Analyzed Reagent," 85%; citric acid monohydrate, Merck, p.a.; mannitol, Merck, p.a.; petroleum, Merck, p.a.

The reagent for catalytic activity experiments was *N*-ethyl formamide (99%) from Fluka. For calibration of the gas chromatograph, propionitrile (99%) from Merck was used.

Gases were from Air Liquide: He 99.995%, H_2 99.9%, and O_2 99.5% pure; they were submitted to no further purification.

Catalysts Preparation and Characterization

Pure MoO_3 or $BiPO_4$ powders with different surface areas were prepared.

MoO_3 "low surface area" ($1.1\ m^2 \cdot g^{-1}$) was prepared by thermal decomposition of ammonium heptamolybdate in air at 500°C for 20 h.

MoO_3 "standard" (with a surface area of $7.9\ m^2 \cdot g^{-1}$) was obtained by "hot petroleum drying" (*8*). A 10 wt% solution of ammonium heptamolybdate in water was emulsified with kerosene. The emulsion was added dropwise to a boiling bath of kerosene; this caused the instantaneous evaporation of water. The solid precursor so obtained was filtered, dried at 200°C for 2 h to eliminate kerosene residue, and subsequently calcined in air at 500°C for 20 h.

$BiPO_4$ "low surface area" ($1.2\ m^2 \cdot g^{-1}$) was obtained by the citrate method (*9*). An aqueous solution of 0.1 *M* $Bi(NO_3)_3 \cdot 5H_2O$ and 0.1 *M* H_3PO_4 in the presence of 6.5 *M* HNO_3 was prepared. The additional nitric acid served to avoid precipitation. Citric acid was added, in such a way that the number of moles of citric acid was equal to the total number of ions of Bi and P. The solution so obtained was evaporated under reduced pressure in a rotary evaporator to form a vitreous amorphous precursor, and the latter was calcined in air at 500°C for 20 h.

$BiPO_4$ "standard" ($8.2\ m^2 \cdot g^{-1}$) was prepared by precipitation, with a 0.05 *M* aqueous solution of $(NH_4)_2HPO_4$, of 0.05 *M* $Bi(NO_3)_3 \cdot 5H_2O$ maintained in solution by complexation with mannitol (molar ratio mannitol/Bi^{3+} = 3/1). $BiPO_4$ was precipitated at room temperature in the form of a very fine colloidal suspension. $BiPO_4$ was separated by centrifugation at 10,000 rpm, washed with water, freeze-dried in order to eliminate the remaining water, and calcined in air at 500°C for 20 h.

Crystal structures of the thus obtained pure oxide phases were characterized by X-ray diffraction (diffractometer Kristalloflex 805 Siemens, using a Ni-filtered Cu*Kα* radiation). Both samples of MoO_3 show the lines characteristic for the orthorhombic phase (*10*). Samples of $BiPO_4$ are both hexagonal (*11*). Surface areas of the single phases were determined gravimetrically (in the same balance described below for the reduction measurements) by N_2 adsorption at 77 K (S_{N_2} = 0.162 nm²/molecule). Total pore volumes, also obtained from adsorption measurements, were negligible in all cases.

As indicated above, several mixing procedures were used.

—Gentle hand-grinding of the mixture of the starting pure phases in an agate mortar for 3 min; by limiting the time of the mechanical mixing, we hoped to minimize changes in morphology and, hence, in texture.

—Dispersion of the starting phases in water, following by water elimination by freeze-drying. The mixing of the suspension of solids was done by means of a mixer ("Ultra-Turrax" from Janke & Kunkel) working at ca. 4000 rpm during 3 min. For freeze-drying, a Freezemobile 12 freezer-drier from Virtis was used.

—Use of a light paraffin (*n*-pentane) instead of water as a dispersing agent. The suspension of solids was cooled to liquid nitrogen temperature. During freeze-drying, the temperature of the evaporating mixture was kept below the melting point of pentane, due to the heat of sublimation of the latter.

The first and third methods were hoped to minimize contamination. The second and third, to minimize physical damage to the individual crystallites.

Powder mixtures of composition

$$r = \frac{MoO_3}{BiPO_4 + MoO_3}$$

(expressed as molar ratio) varying from r = 0 to 1 were prepared.

It was ascertained by X-ray diffraction that the above-described treatments did not modify the crystalline phases present in the solids. In addition, measurements of the surface area of the physical mixtures showed the absence of modification of this parameter: the surface areas of the physical mixtures always amounted to the proper averaged value of those corresponding to the single phases used in the preparation (*12*).

In order to try to detect the possible presence of impurities of one phase on the other, following the mixing treatment, a study combining Analytical Electron Microscopy (AEM), ESCA-XPS, and Ion Scattering Spectroscopy (ISS) was done (*13*). These measurements showed that the samples prepared by cogrinding and by dispersion–freeze-drying in *n*-pentane were constituted of uncontaminated MoO_3 and $BiPO_4$ phases. In the samples prepared by dispersion–freeze-drying in water, the $BiPO_4$ particles were contaminated by a small amount of MoO_3. This can be explained by the fact that, when both powders are put together in water, some amount of molybdate ions can be dissolved (*14*) and deposited on the $BiPO_4$ phase during the freeze-drying procedure.

Catalytic Activity Measurements

Catalytic activities were measured in a

conventional flow apparatus working at low conversion. The reactant (*N*-ethyl formamide) was continuously fed by a syringe pump, vaporized in a preheater (at 200°C) and then carried to the catalytic bed by a mixture of helium and oxygen. The powders described in the previous sections were used as prepared; the catalysts were placed on a sintered glass sealed in the reactor.

Products leaving the reactor were analyzed "on line" by gas chromatography (Intersmat IGC 120 ML); the connection between reactor and chromatograph was maintained at 200°C in order to avoid condensation of the amide. The two GC columns employed contained, respectively: (i) 4% Carbowax 20 M on Anachrom ABS 80–90 mesh (separation of amide, water nitriles and amines) and (ii) Molecular Sieve 5A (separation of O_2, CO, and CO_2). These columns were used alternatively, according to the analysis to be done. Molecular Sieve 5A retained the other components; periodic back-flushing had, thus, to be performed. In both cases, measurements were made with a programmed increase of the column temperature (T_{init} = 50°C; T_{fin} = 200°C; increase: 10°C/min; T detector: 220°C).

Catalytic activities were expressed as percentage conversion (x%), defined as the total percentage of reagent (formamide) transformed. It is not necessary to indicate the selectivities because propionitrile and water were in all cases the only detected products. In addition, material balances confirmed the correspondence between formamide consumption and nitrile formation. Reproducibility in the measurement of conversion was better than 6% of x%.

The flow of reactants is expressed as Liquid Hourly Space Velocity (LHSV), namely, the volume of liquid feed flowing, per hour, over the volume of the catalyst bed:

$$\text{LHSV} = \frac{\text{vol. reagent liquid}}{\text{vol. catalyst} \times \text{h}}$$

Similarly, we define the Gas Hourly Space Velocity (GHSV), used for expressing the flow of oxygen; the volume of the gases is taken at STP.

The set of standard reaction conditions was chosen on the basis of a previous work (*15*). Temperature was maintained at 275°C in order to obtain low conversion and, hence, significant variations of this quantity were obtained when the various parameters were changed. The weight of the catalyst was 0.130 g. The packing density, necessary for calculating the LHSV and GHSV, varied slightly from sample to sample. It was typically 0.85 for a sample of composition $r = 0.5$. The standard reaction conditions were the following: LHSV of *N*-ethyl formamide, 3 h^{-1}; GHSV of oxygen, 4000 h^{-1} (mol O_2/mol of reagent = 4); total GHSV (He + O_2), 64,000 h^{-1}. When the influence of oxygen flow was studied, GHSV of this gas was varied from 8000 to 400 h^{-1}, keeping constant in all experiments the total gas flow to 2.222 $cm^3 \cdot s^{-1}$ (corresponding to the total GHSV of 64,000 h^{-1}).

Thermogravimetric Measurements of Reducibility and Reoxidation

Reduction and some reduction–oxidation measurements were carried out thermogravimetrically in a Setaram MTB 10/8 microbalance connected to a vacuum and gas handling system. Several types of experiments were performed.

In the case of temperature-programmed reductions, the experiments were carried out either under vacuum (10^{-5} mm Hg) or H_2 (500 mm Hg). Prior to each run samples were outgassed at room temperature and 10^{-5} mm Hg for 1 h. In the case of reductions with H_2, the gas was contacted with the solid at room temperature. Thereafter, samples were heated at a linear rate of 10°C/min and weight changes were recorded. Experiments were stopped before reaching 500°C, temperature at which the reduction rate increased very rapidly.

Some cycles were conducted at 400°C in a succession of reducing and oxidizing conditions. For that purpose, heating under vacuum was stopped at 400°C and followed by alternating expositions to oxygen-vacuum.

Isothermal reduction experiments were also carried out. In this case, the samples were evacuated from room temperature to 425°C, then contacted with 500 mm Hg of H_2 and the weight changes were recorded as a function of time at 425°C.

In the reduction with H_2, a liquid-nitrogen trap was used, in order to avoid water readsorption. Changes of pressure due to reaction of H_2 were negligible (<5 mm Hg) because the volume of the balance was large and the weight of the sample small. A verification of the degree of reduction, measured by the weight loss, was possible by reoxidizing the catalyst with O_2 (500 Torr) at 450°C (as in the first step of the redox cycles).

The sample weight was 10 mg in all cases. Results are expressed in the form of percentage weight loss ($-\Delta m\%$). Reproducibility of the measurements was better than 5% of $-\Delta m\%$.

RESULTS

Catalytic Activity

Mechanical mixtures of $BiPO_4$ and MoO_3 exhibit a strong synergy in *N*-ethyl formamide dehydration. This is illustrated by Fig. 1, which concerns "standard" solids (8 $m^2 \cdot g^{-1}$ each). The synergy is observed whichever the method used for mixing the starting powders. There is some influence of the preparation method on the maximum activity observed. The dispersion–freeze-drying in *n*-pentane leads to the highest catalytic activities. All curves pass through a maximum at a value of *r* equal to 0.5. It is to be noted that the shape of these "synergy" curves is not symmetric with respect to the maximum. Higher catalytic activities are observed on the side corresponding to higher MoO_3 contents.

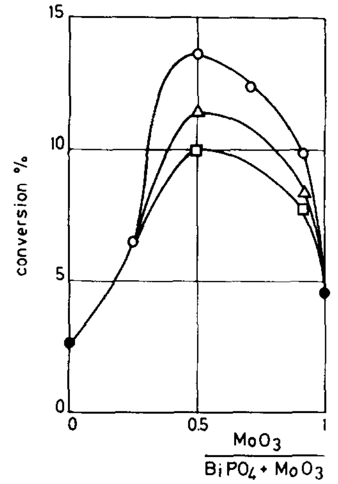

FIG. 1. Catalytic activities at 275°C vs composition of mixtures prepared from MoO_3 and $BiPO_4$ of similar surface areas (±8 $m^2 \cdot g^{-1}$). ○, Joint dispersion–freeze-drying in n-C_5H_{12}; △, joint dispersion–freeze-drying in H_2O; □, joint grinding; ●, single phases.

The second series of results (Fig. 2) concerns catalysts prepared from either $BiPO_4$ or MoO_3 of low surface area and the other phase of the "standard" area by dispersion–freeze-drying in *n*-pentane. The catalytic activity vs composition curves of Fig. 2 also pass through a maximum, but the position of this maximum is displaced toward higher contents of the low surface

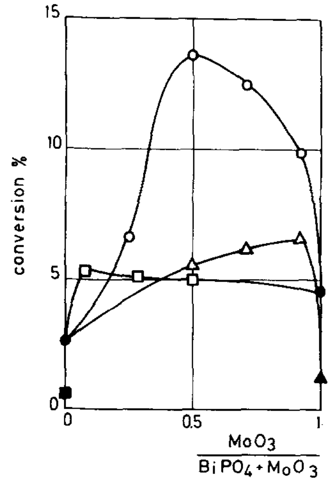

FIG. 2. Catalytic activities at 275°C vs composition of mixtures MoO_3–$BiPO_4$ prepared by dispersion–freeze-drying in n-C_5H_{12} from single phases of various surface areas. ○, MoO_3 "standard" and $BiPO_4$ "standard"; □, MoO_3 "low surface area" and $BiPO_4$ "standard"; △, MoO_3 "standard" and $BiPO_4$ "low surface area"; ●, ■, ▲, single phases.

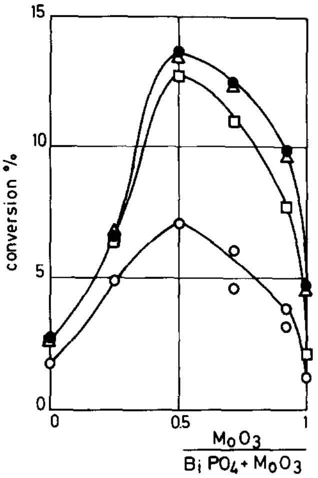

FIG. 3. Influence of oxygen concentration on catalytic activities of mixtures prepared by dispersion–freeze-drying in n-C_5H_{12} of "standard" single phases. O_2 GHSV values are: △, 8000 h^{-1} (O_2/form = 8); ●, 4000 h^{-1} (O_2/form = 4); □, 1000 h^{-1} (O_2/form = 1); ○, 400 h^{-1} (O_2/form = 0.4).

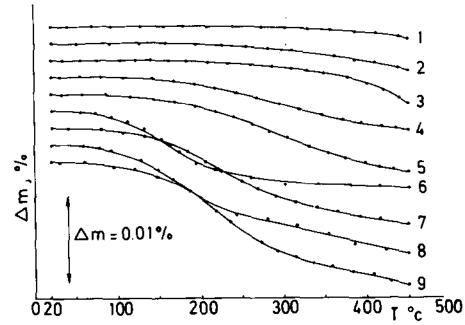

FIG. 4. TG reduction curves under high vacuum. (1) $BiPO_4$ pure; (2) MoO_3 pure; (3) $BiPO_4$ and MoO_3 in separate baskets (equimolecular amounts); (4) mixture obtained by joint grinding; r = 0.500; (5) mixture obtained by joint dispersion–freeze-drying in H_2O; r = 0.500; (6, 7, 8, and 9) mixtures obtained by joint dispersion–freeze-drying in n-pentane, with values of r = 0.250, 0.500, 0.712, and 0.923, respectively.

area phase. The curve of Fig. 1, corresponding to samples prepared from "standard" single-phase powders in n-pentane, has been repeated in Fig. 2. Besides the displacement, we note the difference in sharpness of the maximum and the comparatively low catalytic activities, compared with those of the samples of Fig. 1.

A third series of experiments was carried out in order to clarify the role of oxygen. We used as catalysts the series of mixtures prepared by dispersion–freeze-drying in n-pentane of "standard" MoO_3 and $BiPO_4$ phases. All of the experimental conditions were the same as for the above-reported experiments, except for the oxygen flow that, as indicated in the experimental part, was varied from 8000 to 400 h^{-1}, as expressed as GHSV. The results are given in Fig. 3. It is observed that doubling the quantity of oxygen with respect to standard conditions of operation does not modify the conversion vs catalyst composition curve. But, inversely, lowering the oxygen flow progressively modifies the activity values and, for an oxygen GHSV of 400 h^{-1}, catalytic activities fall to values corresponding to approximately one half of the ones at 4000 h^{-1} O_2, when $r \geq 0.5$. Another feature to be noted is that the effect of oxygen is less pronounced for catalysts contianing less MoO_3 than $BiPO_4$ (low r values).

Thermogravimetric Measurements

In Fig. 4, we present thermogravimetric (TG) results for "standard" single phases and their physical mixtures under high vacuum reduction. For comparison, we include results concerning separated MoO_3 and $BiPO_4$ samples, reduced simultaneously in two separated sample holders attached to the microbalance spring. Similarly, TG results of reduction in H_2 atmosphere (500 mm Hg) are presented in Fig. 5.

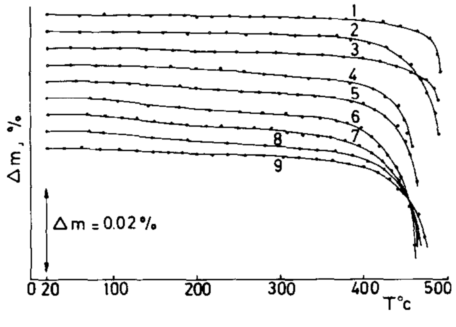

FIG. 5. TG reduction curves under H_2 (500 mm Hg). Same conditions as in Fig. 4.

In both figures, it is easy to observe the higher reducibilities of physical mixtures compared to single phases. Reducibility depends on the preparation method. It varies in parallel with catalytic activity. This remark is more clearly illustrated by Fig. 6, where temperatures necessary to achieve a definite degree of reduction ($\Delta m = -0.005\%$) with H_2 are plotted vs catalyst composition. Curves of Fig. 6 show a shape similar to those of Fig. 1.

The results corresponding to alternating reducing and oxidizing (high vacuum–oxygen) conditions are shown in Fig. 7. The amplitude of weight changes for the mechanical mixtures is much larger than the sum of the effects for the starting separate phases. The amplitude of the weight changes also depends on the value of r (it increases with increasing r) and on the method of preparation. Mixing in n-pentane, that leads to the highest catalytic activities and reducibilities, gave the catalysts showing the most important weight changes in the redox vacuum–oxygen cycles.

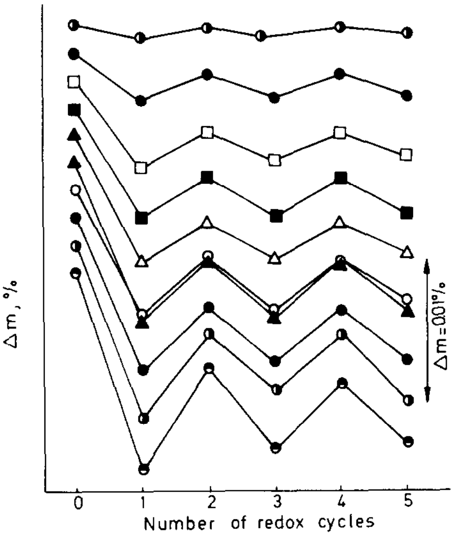

FIG. 7. Redox cycles at 400°C = weight change for the different steps of the cycles; these are: (0) vacuum at room temperature; (1) vacuum, 400°C; (2) O_2 (500 Torr), 400°C; (3) vacuum, 400°C; (4) O_2 (500 Torr), 400°C; (5) vacuum, 400°C. Samples are as follows: ◑, $BiPO_4$ pure; ●, MoO_3 pure; □ and ■, mixtures (joint grinding) with $r = 0.500$ and 0.923, respectively; △ and ▲, mixtures (joint dispersion–freeze-drying in H_2O) with $r = 0.500$ and 0.923, respectively; ○, ●, ◑, and ◒, mixtures (joint dispersion–freeze-drying in n-C_5H_{12} with the respective values of $r = 0.250$, 0.500, 0.712, and 0.923.

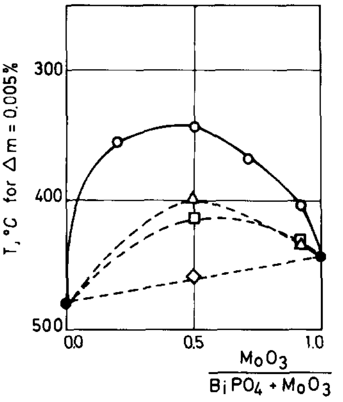

FIG. 6. Temperatures necessary to achieve a reduction corresponding to $\Delta m = -0.005\%$ under H_2 (500 mm Hg) as a function of composition, for mixtures prepared by different methods. ○, joint dispersion–freeze-drying in n-pentane; △, joint dispersion–freeze-drying in H_2O; □, joint grinding; ●, single phases; ◇, $BiPO_4$ + MoO_3 (equimolecular ratio) in separate baskets.

In addition to these effects, it is to be noted that the magnitude of the weight change between two successive reduction–oxidation treatments (or "redox cycles") is different according to the number of redox cycles that the catalyst has previously undergone; i.e., the weight change in reduction in the first cycle is larger than in the second one, and so on. Besides, after successive cycles, the solids progressively lose their ability to reach the original weight before the first redox cycle exposure.

Some thermoprogrammed reduction experiments in H_2 (500 mm Hg) were done with catalysts obtained from MoO_3 and $BiPO_4$ of different surface areas. We deduced a conventional reducibility from the corresponding curves, expressed as the weight loss when temperature reached 400°C. The general trend (Table 1) shows a parallelism between reducibilities and catalytic activities (compare with Fig. 2). In addition, some isothermal (425°C) reduction

TABLE 1

Reducibilities in Hydrogen, of Catalysts Prepared from Single Phases of Different Surface Areas (Percentage Weight Loss at 400°C, in Thermoprogrammed Experiments with a Heating Rate of 10°C/min)

Single starting phases	r	$-\Delta m\%$ (400°C)
$BiPO_4$ "standard"		
MoO_3 "low surface area"	0.923	0.012
" "	0.712	0.010
" "	0.500	0.009
$BiPO_4$ "low surface area"		
MoO_3 "standard"	0.500	0.008
" "	0.250	0.008
" "	0.077	0.007

experiments were performed under H_2 (500 mm Hg) on the most representative samples. These results are shown in Fig. 8, and provide a confirmation of the observed trends. Rates and degrees of reduction clearly depend on the method of mixing and on the ratio of specific surface areas of $BiPO_4$ and MoO_3. They increase in parallel with the catalytic activities.

DISCUSSION

When two phases and several elements are present in catalysts, catalytic activity may, *a priori*, be related (i) to the presence of a given phase, (ii) to a succession of two consecutive reactions (usual bifunctional catalysis), (iii) to a remote control of the active sites of one phase, as described in the introduction, or (iv) to surface promotion of the activity of one phase due to contamination of this phase by minute amounts of the other phase.

Both phases, in the present case, are absolutely necessary for having a good activity (Fig. 1). A succession of two reaction on two different phases is difficult to imagine in the case of formamide dehydration. The intermediary isonitrile is so unstable that one must exclude that it could desorb between the first and second steps of the reaction, namely, before the rearrangement. The contamination of one phase by elements coming from the other phase cannot be absolutely ruled out in the present case, but AEM and ISS did not show any detectable contamination for samples prepared by cogrinding and by dispersion–freeze-drying in *n*-pentane; these techniques showed that some amount of MoO_3 is present in the $BiPO_4$ particles when dispersion–freeze-drying in water was the mixing method (*13*). The fact that the sample where contamination is detected is not the most active catalytically (Fig. 1) seems to rule out the possibility that contamination be responsible for the catalytic synergetic effects we observe in our mechanical mixtures.

We are thus led to take, as a basis of our discussion, the hypothesis of the contact synergy or, more precisely, of the "remote control." The following discussion is presented in this perspective.

1. Catalytic Activity

The assumption underlying the contact synergy hypothesis is that some kind of interaction between the phases is necessary

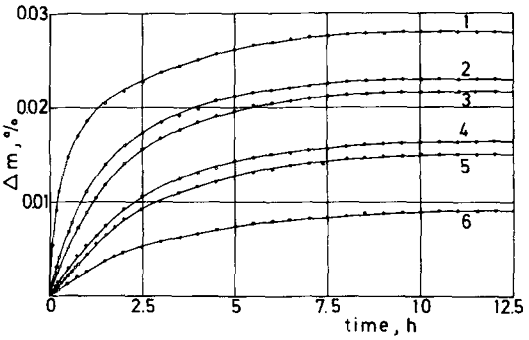

FIG. 8. Isothermal reduction experiments in H_2 (500 mm Hg) at 450°C. (1–3) Mixtures with $r = 0.500$, obtained from "standard" single phases by joint dispersion–freeze-drying in $n\text{-}C_5H_{12}$, joint dispersion–freeze-drying in H_2O and joint grinding, respectively; (4) mixture with $r = 0.500$ obtained from MoO_3 "low-surface-area" and $BiPO_4$ "standard"; (5) single-phase MoO_3 "standard"; (6) mixture with $r = 0.500$ obtained from MoO_3 "low surface area" and $BiPO_4$ "standard" (4 and 6 by dispersion–freeze-drying in $n\text{-}C_5H_{12}$).

for the catalytic action to take place. More precisely, in the frame of the remote control theory, the activity of sites on one phase is controlled by some action of the other phase. Then, in a quite general way, two independent parameters will determine the intensity of this interaction or remote control effect.

The first parameter is the ratio between the surface areas developed by the two different phases. This ratio has necessarily an influence if some surface phenomenon takes place on each phase. The displacement of the maxima observed in Fig. 2 is an evidence that the relative surface areas of the two mixed powders, rather than the bulk composition, is at stake in the synergy. The maximum activity is obtained when the total surface area developed by one phase is comparable to that developed by the other phase.

The second important parameter is the number and intimacy of contacts between the particles of the two different phases. This results from the fact that the nature of the contact may influence the passage of the mobile species from one phase to the other.

The first aspect which characterizes the contacts is their number. If some contact synergy is operating during catalysis, a maximum effect should be observed when the particles of the two phases are perfectly interdispersed, statistically. This ideal situation maximizing the synergetic effects cannot be easily achieved in practice, due mainly to the presence of aggregates in each of the starting powders. These aggregates, of various strengths, have to be broken for achieving good interdispersion. The more effective the mixing procedure, the larger the number of aggregates which will be broken.

The other aspect to be considered, is the quality of the contact between neighbor particles of different nature. This quality includes proximity of the surfaces in contact, extent of contact, and, possibly, nature of impurities trapped between the contacting surfaces. The quality of the contact between $BiPO_4$ and MoO_3 in our experiments certainly depends on the mixing procedure.

For these reasons, one should expect some variation of the effects experimentally observed, according to the method used for mixing the starting powders. Our results indicate such variations (Fig. 1). The gentle grinding of the starting phases is expected to be the method leading to the poorest degree of interdispersion; in fact, this is the method leading to the lowest catalytic activities.

In previous studies in our group (*3, 15*), BiPMo oxides prepared by coprecipitation had been used. In that case, the maxima appeared for $r = 0.923$. The explanation for that lies in the fact that, in samples prepared by coprecipitation, the MoO_3 has a very small surface area compared to that of $BiPO_4$. If the contact synergy phenomenon exhibited by the system demands that the total surface area developed by MoO_3 must be nearly the same as that of $BiPO_4$ in order to achieve an optimal activity as suggested by Fig. 1, the optimal total weight (or molar proportion) of MoO_3 had to be high, in a way similar to the case of our mechanical mixtures using a low-surface-area MoO_3.

We tested a sample of a "bismuth phosphomolybdate," prepared by coprecipitation according to the technique described in (*3*), in the same experimental conditions as for the other catalysts studied in the present work ($T = 275°C$). We obtained a conversion of 11.97%. But it is necessary to take into account the specific surface area of the samples. The coprecipitated sample had a surface area of only $1.64\ m^2 \cdot g^{-1}$, compared to $8\ m^2 \cdot g^{-1}$ for the samples whose activity is reported in Fig. 1. Values of conversion per unit surface area, assuming a linear relationship between conversion and surface area, are presented in Table 2. Conversion per square meter ($x\% \cdot m^{-2}$) value for the catalyst prepared by coprecipitation with a molar ratio Bi : P : Mo of 1 : 1 : 12 amounts to $7.3\% \cdot m^{-2}$. This value is much higher than that of $1.72\% \cdot m^{-2}$ obtained for the

TABLE 2

Catalytic Activities Expressed as Conversion per Square Meter of Surface Area ($x\% \cdot m^{-2}$) for Catalysts Prepared from "Standard" ($8\ m^2 \cdot g^{-1}$) Single Phases

Sample	Method of mixing	r	$x\% \cdot m^{-2}$
MoO_3 pure	—	1.0	0.585
$BiPO_4$ pure	—	0.0	0.32
MoO_3 "std"–$BiPO_4$ "std"	Disp.–freeze-drying in n-C_5H_{12}	0.923	1.24
" "	" " "	0.712	1.56
" "	" " "	0.500	1.72
" "	" " "	0.250	0.84
" "	Disp.–freeze-drying in H_2O	0.923	1.06
" "	" " "	0.500	1.48
" "	Cogrinding	0.923	0.98
" "	" " "	0.500	1.24
BiPMo oxide	Coprecipitation	0.923	7.30

most active mechanical mixture ($r = 0.5$, prepared by dispersion–freeze-drying in n-pentane).

The comparison between coprecipitated sample and mechanical mixtures suggests that the extent of contact between $BiPO_4$ and MoO_3 is critical. The two phases present in coprecipitated catalysts (*3*, *15*) result from the segregation of a homogeneous precursor containing Bi, P, and Mo. Salts of phosphomolybdic acid usually retain their identity, namely, their homogeneity at an atomic level, until temperatures of around 300°C or slightly more (*16*). The two-phase catalysts obtained by coprecipitation and calcination at 600°C (*15*) result from a segregation of the phases in the solid state, which necessarily maximizes the interdispersion of the resulting phase. It is thus logical that, in this case, the synergy between the phases is much more efficient than in catalysts prepared by mixing, where large aggregates of each phase, each containing many particles, are present.

The comparison above was between the coprecipitated catalyst of composition $r = 0.92$ and our mechanical mixture of composition $r = 0.5$. This comparison was relevant since, in each catalyst, the surface area developed by $BiPO_4$ and MoO_3 were comparable. It is also interesting to compare catalysts of the same overall composition ($r = 0.92$). A mechanical mixture of that composition, prepared from "standard" surface area phases gave an activity of $1.24\% \cdot m^{-2}$ (Table 2). It is still more instructive to compare with a mechanical mixture prepared with "low-surface-area" MoO_3 (Table 3). The coprecipitated sample and this mechanical mixture were quite comparable in surface area (respectively, 1.65 and $1.64\ m^2 \cdot g^{-1}$) and in difference of specific surface area between $BiPO_4$ and MoO_3. However, the coprecipitated sample was twice as active as the mechanical mix-

TABLE 3

Catalytic Activities Expressed as Conversion per Square Meter of Surface Area ($x\% \cdot m^{-2}$), for Catalysts Prepared from Single Phases of Different Surface Areas (Dispersion–Freeze-Drying in n-C_5H_{12})

Sample	r	$x\% \cdot m^{-2}$
MoO_3 "standard"	1.0	0.585
MoO_3 "low surface area"	1.0	1.21
$BiPO_4$ "standard"	0.0	0.32
$BiPO_4$ "low surface area"	0.0	0.54
MoO_3 "standard"	0.077	2.95
+ $BiPO_4$ "low surface area"	0.250	1.76
	0.500	1.07
MoO_3 "low surface area"	0.500	1.14
+ $BiPO_4$ "standard"	0.712	1.88
	0.923	3.67
BiPMo oxide (coprecipitation)	0.923	7.30

ture (Table 3). This must be attributed to the less perfect interdispersion achieved in the mechanical mixture.

All results thus seem to support our view that a contact synergy and a remote control mechanism are operating in the dehydration of *N*-ethyl formamide on Bi–P–Mo catalysts. Clearly, the number and intimacy of contacts between the particles of the two phases are important parameters. Mechanical mixing seems to be relatively ineffective in breaking the microaggregates in each powder. The methods using dispersion of the powders in a liquid are more effective in this respect. But the samples obtained by coprecipitation, whose structure is a consequence of segregation from an initially homogeneous precursor, contain still more such contacts.

Our results also suggest other features of the suspected remote control mechanism operating during catalysis. Returning to Fig. 1, we note that the conversion–composition curves are not symmetrical with respect to the maxima. Higher conversions are observed for samples rich in MoO_3. This suggests that the roles of $BiPO_4$ and MoO_3 in the synergy are quite different. The same effect is much clearer in Fig. 3, where the effect of diminishing oxygen concentration on catalytic activities turns out to be stronger for catalysts with $r \geq 0.5$. The fact that the MoO_3 phase is so sensitive to oxygen partial pressure suggests that this is the phase that carries active centers for the formamide dehydration, while the $BiPO_4$ phase modulates the activity of MoO_3 by sending an activated oxygen species on that phase (remote control effect). On the other hand, it is interesting to note the existence of a large interval of oxygen concentrations (1000 to 8000 h^{-1} GHSV O_2) where catalytic activity remains almost unchanged; this can be explained by the existence of a saturation phenomenon, when oxygen concentration amounts to more than 1000 h^{-1} GHSV. These high concentrations of oxygen would suffice to produce enough oxygen mobile species to maintain catalytic activity and selectivity of the MoO_3 phase.

2. *Reactions under Vacuum, with Hydrogen and with Oxygen*

The results of Figs. 4 and 5 show that, either under vacuum or in a H_2 atmosphere, reducibilities of mechanical mixtures are higher than those of single phases, and they vary with the mixing method in the same way as catalytic activities. Isothermal reduction experiments (Fig. 8) support the results obtained in temperature-programmed reduction. It can be concluded that there is a parallelism between catalytic activity for *N*-ethyl formamide dehydration and oxidizing capacity of the mechanical mixtures MoO_3–$BiPO_4$.

When reductions are done under H_2 atmosphere, MoO_3 is reduced to MoO_2, as it is well known from the literature (*17*). $BiPO_4$ can also be reduced, but at higher temperatures (500°C) to give metallic Bi, with some amount of elemental P (*18*). In the conditions of the thermoprogrammed reduction experiments done in this work, pure MoO_3 and pure $BiPO_4$ are reduced. It is to be expected that in the mixture, both are also reduced, but we cannot say whether both phases activate the reduction of the other.

In the case of the reduction under a high vacuum, MoO_3 is the phase that can be expected to be reduced the more easily. Indeed, EPR spectra of the solids studied in this work showed the presence of high amounts of Mo^{5+} alter reduction under vacuum under mild conditions (250°C) (*12*). This can be due to an initial appearance of oxygen vacancies at the surface of the solid, followed by a reorganization of the structure through the formation of shear phanes (*19*).

When alternate reducing and oxidizing treatments are done (Fig. 7), the amplitude of weight changes is the largest for the most reducible (Fig. 4) and catalytically most active mechanical mixtures (Fig. 1). This shows again the influence of phase contact or reducibility, and the probable simility of the involved mechanisms.

The fact that catalysts progressively lose their capacity to be reoxidized can be related to the ability of the solids to form stable partially reduced structures, which can be realized by the formation of shear planes near the surface. The degree of reduction remains, however, extremely low in our experiments. The loss of weight which would be brought about by the reduction of MoO_3 to a suboxide would range between 0.42% ($Mo_{13}O_{28}$) to 0.69% (Mo_8O_{23}), supposing MoO_3 represents *half* the weight of the investigated $BiPO_4$–MoO_3 mixtures. These values have to be compared with those reported in Figs. 4 to 8 (ca. 0.03% at a maximum). Only less than 10% of MoO_3 thus seems to be transformed to a suboxide. No important structural transformation in the bulk can occur, and certainly not as deep as that leading to MoO_2 (*20*).

Data on the reducibility in H_2 atmosphere for the mechanical mixtures prepared from single phases of very different surface areas are not as conspicuous as those presented in Figs. 4 to 6 (in a similar way, maxima for activity in Fig. 2 are not very pronounced).

The experiments involving reduction–reoxidation cycles show a very important phenomenon, namely, that the rates of *oxidation* of the partially reduced solids also vary in parallel with the reducibility (Fig. 7). The variation of the rates of all these solid-state reactions show a strong parallelism with the variation of the rate of the catalytic reaction with catalyst composition. This strongly suggests that a common mechanism is involved. The possible mechanisms will be discussed in the following sections.

3. *Mechanism*

Putting together the results in catalysis and in reduction and reoxidation experiments, a possible picture of the catalytic working sites would be that of a solid slightly reduced on the surface, whose reduction would be limited in extent by continuous reoxidation. The reactant, namely, *N*-ethyl formamide, would continuously tend to reduce the catalysts, whereas oxygen would limit the degree of reduction.

Our hypothesis is that the majority of the active sites is located on MoO_3, and that its activity is *controlled* (in the sense of the remote control theory) by the $BiPO_4$ phase. Oxygen would be activated (probably dissociated) on $BiPO_4$ and would migrate, or "jump," on to MoO_3. The exact mechanism might either be surface spill-over, or migration through the lattice and transfer from the $BiPO_4$ lattice to that of MoO_3. The mobile oxygen species would be capable of reoxidizing the surface of MoO_3 to the proper active state. This would be done continuously during catalysis. The higher rate of reoxidation of mixtures in reduction–oxidation cycles substantiates this possibility.

It is logical to assume that, under vacuum or in hydrogen, the inverse flow could take place. Such a "reverse spill-over" is observed in the case of hydrogen. It is the normal consequence of the mobility of a species on a surface. It suffices to reverse the chemical (or electrochemical) potential gradient of the mobile species to reverse the direction of the driving force. And it ensues from the "microscopic reversibility" principle that an active center, if active in dissociating a molecular species and producing a mobile surface species, should also catalyze the recombination. The reverse spill-over implies that, in the reduction experiments, oxygen coming from MoO_3 is a surface mobile species or transforms easily into such a species and migrates to $BiPO_4$. In the experiments under a high vacuum, the mobile species would recombine to molecular oxygen on the active sites of $BiPO_4$. In the experiments with hydrogen, a more complicated mechanism would take place. Our experiments strongly suggest that sites active in the reaction of mobile oxygen with H_2 are also carried by $BiPO_4$.

We suspect that additional information is hidden in the shape of the synergy curves of Fig. 1, especially in the asymmetry of these curves, as well as in the various responses to differences in oxygen partial pressure during catalysis (Fig. 3). We are presently investigating our mechanism to account for this effect.

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