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

## III. An ESR Study of Reduction Properties of the Mixtures of $MoO_3$ and $BiPO_4$

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A study of the interactions between $MoO_3$ and $BiPO_4$ in mixed oxide catalysts active in *N*-ethyl formamide dehydration was made by determining the Mo(V) Electron Spin Resonance (ESR) signal intensities after reduction, under different conditions, of mechanical mixtures of separately prepared $BiPO_4$ and $MoO_3$. The signal intensity clearly depended on the intimacy of contact, the reducibility of $MoO_3$ in mechanical mixtures being higher than in pure $MoO_3$. The mixing method in which both powders were dispersed together in *n*-pentane was the most effective. Alternate reducing and oxidizing treatments showed that the reaction was reversible at high temperature. After comparison of the ESR results with catalytic activities, it is concluded that, during catalysis, reoxidation by oxygen of the $MoO_3$ surface is necessary to counterbalance the reducing effect of formamide, thus restoring the catalytically active sites. © 1986 Academic Press, Inc.

## INTRODUCTION

This paper is the third of a series (*1*, *2*) concerning $BiPO_4$–$MoO_3$ catalysts, their activity in the dehydration of formamides to nitriles in the presence of molecular oxygen, their characterization, and the modifications they undergo in reducing or oxidizing atmospheres.

In the first paper of the series (*1*) we showed that $BiPO_4$ and $MoO_3$ particles acted synergetically in the catalytic dehydration of formamides. The discussion of this synergy and of the role of oxygen led us to interpret the results as the consequence of a *remote control* effect, namely, to suppose that molecular oxygen was dissociated on $BiPO_4$ to a mobile oxygen species ("spill-over oxygen"), which migrated onto the surface of $MoO_3$, where it created (or regenerated) the catalytic sites active for dehydration. This interpretation led us to infer that the presence of $BiPO_4$ could accelerate the reoxidation of a previously reduced $MoO_3$ surface. As spill-over phenomena are usually reversible ("reverse spill-over"), it was also thought that superficial or mild bulk reduction of $MoO_3$ could take place more rapidly when $BiPO_4$ was present. The results reported in that first paper strongly supported these conclusions.

The second paper (*2*) dealt with the physicochemical characterization of the mixtures of powders used as catalysts. One of the main objectives was to investigate whether material from one phase could contaminate the other phase. If, indeed, $MoO_3$ contamines $BiPO_4$, one could argue that no remote control mechanism is necessary for explaining the results, but that the observed enhanced catalytic activity is due to new surface active centers associating Mo with $BiPO_4$. Contamination could be detected in one preparation (freeze-drying after suspension of the powder in water), which was not the most active. Experimental evidence is that contamination does not explain the synergy.

According to our interpretation, the num-

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TABLE 1

Single Phases Used in Catalyst Preparation

| Phase | $S$ ($m^2$ $g^{-1}$) | X-Ray pattern |
|---|---|---|
| $BiPO_4$ "low surface area" | 1.2 | Hexagonal |
| $BiPO_4$ "standard" | 8.2 | Hexagonal |
| $MoO_3$ "low surface area" | 1.1 | Orthorhombic |
| $MoO_3$ "standard" | 7.9 | Orthorhombic |

ber of active sites, supposed to be situated, in their majority, on the surface of $MoO_3$, depended on the oxidation–reduction state of that surface, too reduced a surface corresponding to inactivated $MoO_3$, and reoxidation by spill-over oxygen bringing about the formation or regeneration of the active sites. Electron Spin Resonance (ESR) is an extremely sensitive method for probing these reduction–oxidation changes, as it easily detects Mo(V). It was thus logical to continue our investigations using ESR. This paper deals the corresponding results. Thus, we hoped to give a more complete picture of the factors which explained our first results on the Bi–P–Mo–O system (*3*–*6*).

We also could expect to detect anomalous Mo signals if Mo contamination of the $BiPO_4$ surface took place. In that case, Mo would be in an environment different from its environment in $MoO_3$, and this could, in principle, bring about changes in the Mo(V) signals. Actually, the following results will indicate that the Mo(V) signals are normal. The conclusion is thus that ESR does not detect abnormal Mo attributable to contamination. This absence of evidence cannot be the object of much discussion. The problems of contamination, therefore, will not be considered in what follows.

## EXPERIMENTAL

*Catalyst preparation and characterization.* Catalyst preparation and characterization have been described in the previous publications of the series (*1*, *2*). It will therefore suffice to say that catalysts were prepared by gently mixing separately synthesized powders of $BiPO_4$ and $MoO_3$. Three methods were used: (i) gentle cogrinding in a mortar; (ii) suspension in water, stirring, and freeze-drying; (iii) suspension in *n*-pentane, stirring, and evaporation. Two samples of each oxide ($BiPO_4$

TABLE 2

Characteristics of Physical Mixtures

| Starting phase | Method of mixing | $r$ | $S_{BET}$ ($m^2$ $g^{-1}$) | $S_{av}$[a] ($m^2$ $g^{-1}$) |
|---|---|---|---|---|
| $BiPO_4$ "standard" | Cogrinding | 0.923 | 8.0 | 7.94 |
| $MoO_3$ "standard" | | 0.500 | 8.1 | 8.10 |
| $BiPO_4$ "standard" | Dispersion–freeze- | 0.923 | 7.9 | 7.94 |
| $MoO_3$ "standard" | drying in $H_2O$ | 0.500 | 7.8 | 8.10 |
| | | 0.923 | 7.9 | 7.94 |
| $BiPO_4$ "standard" | Dispersion–freeze- | 0.712 | 8.0 | 8.04 |
| $MoO_3$ "standard" | drying in *n*-pentane | 0.500 | 8.1 | 8.10 |
| | | 0.250 | 8.1 | 8.16 |
| $BiPO_4$ "standard" | Dispersion–freeze- | 0.923 | 1.8 | 2.17 |
| $MoO_3$ "low surf. area" | drying in *n*-pentane | 0.712 | 3.3 | 4.37 |
| | | 0.500 | 4.9 | 5.92 |
| $BiPO_4$ "low surf. area" | Dispersion–freeze- | 0.500 | 4.7 | 3.35 |
| $MoO_3$ "standard" | drying in *n*-pentane | 0.250 | 2.9 | 2.11 |
| | | 0.077 | 1.8 | 1.45 |

[a] $S_{av}$ is the properly averaged value calculated from the surface areas of single phases of departure (given in Table 1), taking into account the weight fractions, $s$ and $1 - s$, of the phases in the mixtures: $S(av) = sS_{BiPO_4} + (1 - s)S_{MoO_3}$.

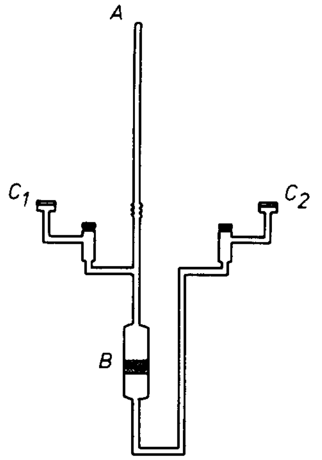

FIG. 1. Scheme of the special cell used for sample treatments under controlled conditions. (A) Tube for ESR measurements; (B) sintered-glass catalyst holder; (C) greaseless valves and stopcocks.

and $MoO_3$), one with "standard" surface area (±8 $m^2$ $g^{-1}$) and one with low surface area (±1 $m^2$ $g^{-1}$) were prepared (Table 1). Samples of different composition, measured by $r = MoO_3/(MoO_3 + BiPO_4)$ (molar ratio) were prepared (Table 2).

*ESR measurements.* Electron spin resonance measurements were performed with X-band Varian E-12 spectrometer equipped with a double cavity, using 100-kHz modulation frequency and 20-mW incident microwave power. Measurements at temperatures other than ambient (+300 to −196°C) were made using the Varian variable-temperature accessory. To allow for quantitative comparisons between the spectra, the signal intensities were normalized to the signal intensity of the standard Varian "strong pitch" sample; this made allowance for error sources because we kept constant a common set of instrumental parameters, i.e., microwave power and modulation amplitude. These parameters were chosen as to avoid signal deformation and saturation phenomenon. The plot of signal intensity versus the square root of power is linear up to 200 mW at the temperatures of investigation.

Pretreatment of the samples and ESR measurements were done using the special device represented in Fig. 1. The device was composed of an ESR cell constituted of a 3-mm-i.d. tube of pure quartz (A), a 10-mm-o.d. tube with a sintered glass (B) containing the catalyst during pretreatment, and greaseless valves. It could be attached in $C_1$ and $C_2$ to a gas manifold equipped with greaseless stopcocks and connections and a liquid-nitrogen trap placed nearby the cell. After the catalyst, in position B, had been submitted to one of the treatments described below, the cell was removed and inverted from the position in Fig. 1; the catalyst was thus transferred to the bottom of the ESR tube and the ESR measurements were done. In some cases the system was reattached to the gas manifold, the catalyst was subjected to a new treatment, and another determination of the ESR spectrum was made. The ESR quartz tube (A), for each determination, was filled to a height of at least 4 cm (largely exceeding the length probed in the measurements). The packing of the powder was taken to be constant as blank experiments showed similar packing densities for $MoO_3$, $BiPO_4$, and their mixtures studied in this work.

*Pretreatments.* About 1 g of catalyst was submitted to one of the four following treatments (i) outgassing under high vacuum at room temperature and then at 250 or 450°C for 1 h; (ii) outgassing under high vacuum at room temperature and then exposing at 250°C to hydrogen at 500 mm Hg for 1 h. In some cases, hydrogen was removed if present and oxygen added (500 mm Hg) the temperature being raised again to the desired value; (iii) alternating cycles, at 250°C, of reducing ($H_2$, 500 mm Hg) and oxidizing ($O_2$, 500 mm Hg) conditions (the ESR signals were recorded following each step); (iv) catalytic reaction conditions, in which the sample was exposed to *N*-ethyl formamide (LHSV = 3 $h^{-1}$) in absence or presence of oxygen (GHSV = 4000 $h^{-1}$). The catalyst was then purged of organic molecules with a flow of helium at the reaction temperature of 275°C for 5 min.

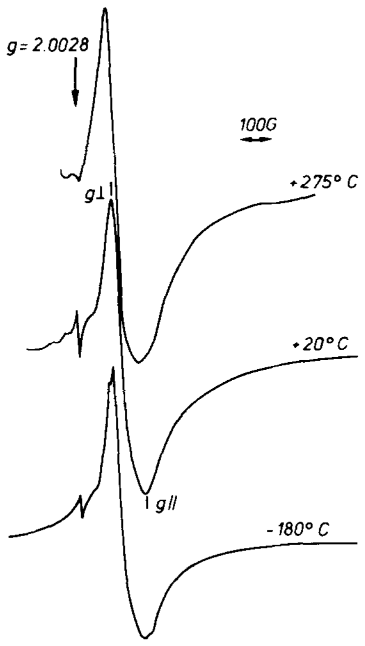

FIG. 2. Typical Mo(V) spectra measured at different temperatures on a catalyst ($r$ = 0.5000) prepared by dispersion–freeze-drying in $n$-pentane after reduction in $H_2$ (300 mm Hg) at 250°C for 1 h.

## RESULTS

Molybdate catalysts have been widely investigated by ESR to study the changes in the oxidation degree of molybdenum ions occurring during the catalytic process ((*7*) and references therein). The ESR spectra of Mo(V) species observed in our catalysts reduced either by heating under hydrogen or under vacuum are shown in Fig. 2. An axially symmetrical spectrum with $g_\parallel$ = 1.88 and $g_\perp$ = 1.94 is obtained for all catalysts investigated in this work. No change of signal intensity is observed for reducing treatment times larger than 1 h. The relative intensity varies with the mixing procedure. This point will be discussed later. The shape of the signal does not show appreciable temperature dependence and it is detectable even at 275°C. If molecular oxygen is allowed to adsorb on the reduced catalyst, at room temperature, the Mo(V) signal intensity remains practically unchanged. It is diminished when the sample is heated in an oxygen atmosphere at 250°C. The Mo(V) species formed after high vacuum reduction at 450°C are more resistant to reoxidation at high temperature. No signal attributable to oxygen species has been observed, even at the liquid-nitrogen temperature. For the catalysts prepared with the mixing procedure using $n$-pentane as dispersing agent, a narrow and symmetrical signal appears at $g$ = 2.0028. This signal, which is probably due to a polycondensed carbonaceous residue will not be discussed further as its intensity does not show any correlation with other parameters.

The relative intensity of the Mo(V) species measured after reduction in $H_2$ at 250°C for 1 h, is plotted in Fig. 3, versus the molar ratio $r$ of $MoO_3$–$BiPO_4$ mechanical mixtures prepared with "standard" area solids following the "grinding" (□) or the "dispersion–freeze-drying" in $H_2O$ (△) or in $n$-pentane (○) procedure. Results obtained for similar catalysts treated under high vacuum at 250 and 450°C are reported in Figs. 4 and 5. Some experiments were repeated, the reported points on the graph correspond to the averaged values and the

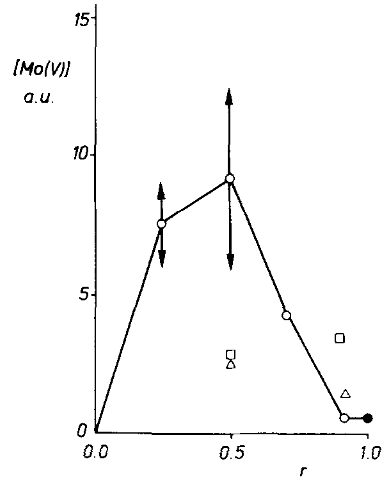

FIG. 3. Intensities of Mo(V) signals measured in catalysts prepared from "standard" single phases after reduction in $H_2$ (300 mm Hg) at 250°C for 1 h. The methods of preparation were: ○, dispersion–freeze-drying in $n$-pentane; △, dispersion–freeze-drying in $H_2O$; □, Cogrinding; ●, single phase.

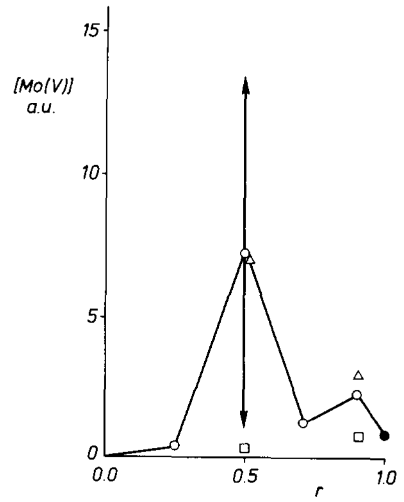

FIG. 4. Intensities of Mo(V) signals measured in catalysts prepared from "standard" single phases after high-vacuum reduction at 250°C for 1 h. Same symbols as for Fig. 3.

vertical bar indicates the dispersion of the results.

Despite the poor reproducibility in some circumstances, of the repeated measurements, one concludes that the method of dispersion–freeze-drying in $n$-pentane gives rise to higher Mo(V) intensity values compared to the values obtained with co-ground solids. The highest values are always observed in the range of $r$ around 0.5. The kind of reduction treatment used does not seem to affect too much the amount of Mo(V) species produced when one compares the results for similarly mixed preparations.

The influence of the surface area of both phases on the reducibility of the catalyst is shown in Fig. 6 where the relative intensity of the Mo(V) signal is plotted against the molar ratio $r$ for solids mixed by the dispersion–freeze-drying in $n$-pentane method and reduced in $H_2$ at 250°C for 1 h. Those points of Fig. 3 corresponding to the "standard" phases are reproduced here for the comparison (O). Similar graphs are obtained for catalysts reduced under high vacuum at 250 or 450°C. The highest Mo(V) intensity measured moves toward high molar contents of the low-surface area phase.

A sample prepared by dispersion–freeze-drying in $n$-pentane with an $r = 0.5$ value, from "standard" phase mixture, and submitted to cycles of reducing ($H_2$)–oxidizing ($O_2$) conditions, gives an evolution of the Mo(V) signal as shown in Fig. 7. Each cycle

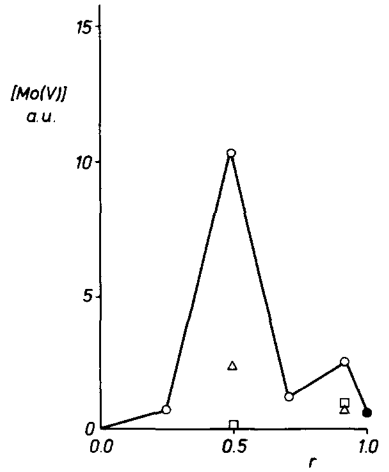

FIG. 5. Intensities of Mo(V) signals measured in catalysts prepared from "standard" single phases after high-vacuum reduction at 450°C for 1 h. Same symbols as for Fig. 3.

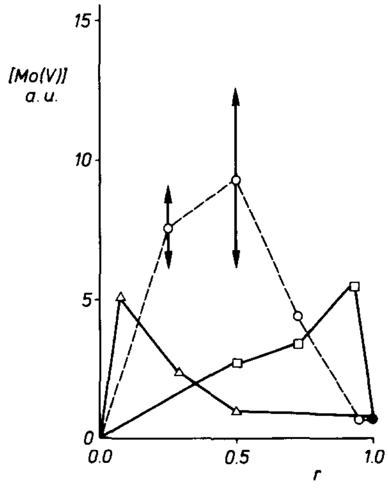

FIG. 6. Intensities of Mo(V) signals measured in catalysts prepared from single phases of different surface areas after reduction in $H_2$ (300 mm Hg) at 250°C for 1 h. O, $MoO_3$ "standard" and $BiPO_4$ "standard"; △, $MoO_3$ "standard" and $BiPO_4$ "low surface area"; □, $MoO_3$ "low surface area" and $BiPO_4$ "standard."

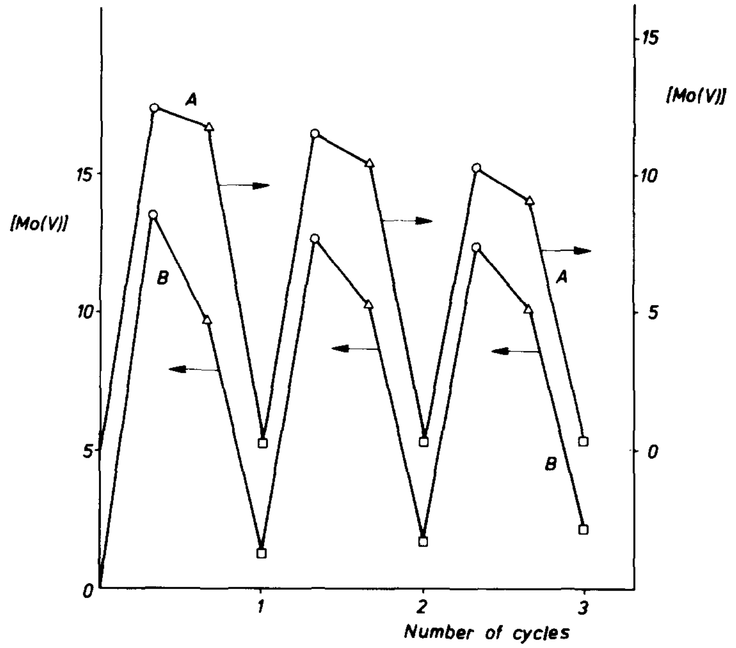

FIG. 7. Intensities of Mo(V) signals measured after reducing–oxidizing cyclic treatments on a catalyst $r = 0.500$ prepared by dispersion–freeze-drying in *n*-pentane. *A* (upper curve): ○, $H_2$, 250°C, 1 h; △, high vacuum, room temperature (r.t.) + air, r.t., 1 h; □, air, 250°C, 1 h. B (lower curve): ○, high vacuum, 250°C, 1 h; △, air, r.t., 1 h; □, air, 250°C, 1 h.

gives three values corresponding to the sample first exposed to $H_2$ at 250°C for 1 h, then evacuated and exposed to $O_2$ at room temperature, and finally maintained at 250°C during 1 h under $O_2$ atmosphere (Fig. 7A). From cycle to cycle, progressive loss of the original Mo(V) intensity is observed, this fact being less marked with a $H_2$–air cycle. Successive high vacuum–$O_2$ cycles produced the same trend, although the relative intensity of the Mo(V) signal remaining after $O_2$ exposure at high temperature increased with the number of cycles (Fig. 7B).

Samples similar to the one used in the alternate reducing oxidizing conditions have been exposed to *N*-ethyl formamide under catalytic reaction conditions. The Mo(V) relative signal intensities corresponding to the various experimental treatments are reported in Table 3. The values are enhanced when the sample is subjected to catalytic reaction conditions in the absence of oxygen. On the contrary, the absence of formamide in the reacting medium prevents Mo(V) formation; reduced ions that had appeared previously in the course of the catalytic reaction are reoxidized as soon as oxygen is present.

A sample of a "bismuth phosphomolyb-

TABLE 3

Mo(V) ESR Signal Intensities after Exposure to "Standard Reaction Conditions" (SRC) (see Experimental) of a Catalyst with $r = 0.500$ Prepared from $MoO_3$ "Standard" and $BiPO_4$ "Standard" by Dispersion–Freeze-Drying in *n*-Pentane

| Type of treatment | [Mo(V)] (a.u.) |
|---|---|
| Without any treatment | 0.13 |
| SRC (1 h) + He flow | 1.26 |
| SRC (1 h) + formamide flow (1 h) + He flow | 3.97 |
| SRC (1 h) + $O_2$ flow (1 h) + He flow | 0.22 |

date," prepared by coprecipitation according to the technique described in (*4*), was tested under the same experimental conditions ($H_2$, 250°C, 1 h). The comparison is relevant since the surface areas developed by the $BiPO_4$ and the $MoO_3$ phases are comparable in the coprecipitated catalyst of composition $r = 0.92$ and the mechanical mixture of composition $r = 0.5$. The Mo(V) signal recorded for the coprecipitated sample was three times more intense than the highest value obtained in the case of the mechanical mixture. This result supports further that the extent of the contact between $BiPO_4$ and $MoO_3$ is a critical parameter. The "two-phase" catalysts obtained by coprecipitation maximize the interdispersion of the resulting phases.

The results obtained under alternate reducing–oxidizing conditions (Figs. 7A and B) show that formation of Mo(V) in these samples is reversible although successive cycles cause a progressive loss of the capacity of the sample to recover its initial oxidation state. It is observed that oxygen acts as an oxidant for these Mo(V) ions. At 250°C in oxygen atmosphere Mo(V) signal intensity is reduced to less than 10% of its initial value. The lack of the signal decrease after oxygen adsorption at room temperature suggests a large bulk reduction.

## DISCUSSION

The ESR parameters of the molybdenum ions observed in this work fall within the range of the values currently reported for molybdenum catalysts, previously studied (*7*, *8*). The results presented in Fig. 3 show that the reducibility of the Mo(VI) ions depends on the method of mixing and is enhanced in the dispersion–freeze-drying in *n*-pentane procedure. These results underline the influence of the $BiPO_4$ phase and the reducibility of these catalysts compared to a single-phase $MoO_3$ solid. The intensity of the Mo(V) signal is not simply determined by the amount of $MoO_3$ added to the mixture. The results in Fig. 6 indicate moreover that the surface area of the phase in presence is an important parameter.

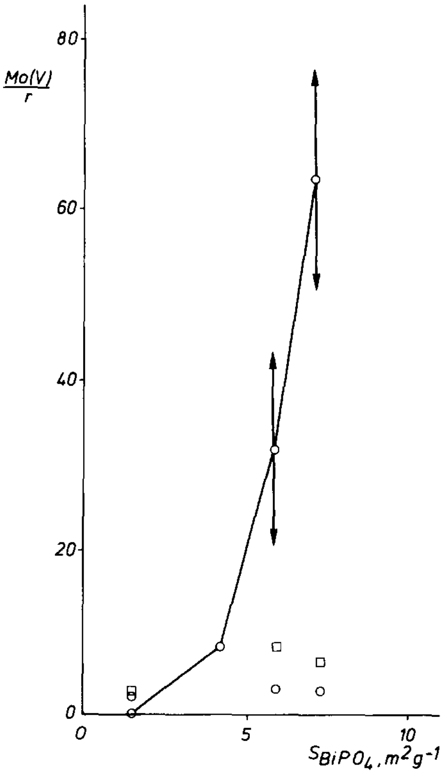

FIG. 8. Intensity of Mo(V) ESR signals normalized to total $MoO_3$ [Mo(V)/*r*] vs $BiPO_4$ surface area in contact with $MoO_3$. This intensity is proportioned to Mo in the $Mo^{5+}$ state.

The reducibility and the catalytic activities in formamide dehydration were shown to be higher than those of single phases and varying with the mixing method in a similar fashion (1). The ratio between the surface areas developed by the two different phases and the intimacy of contacts between the particles were shown to be critical parameters in this work. It is worth to note that in ESR, similarly, the maximum intensity of the Mo(V) signal is obtained when the total surface area developed by one phase is comparable to that developed by the other phase. In this respect, Fig. 8 shows the value of the Mo(V) intensity normalized to the relative amount of $MoO_3$ phase present in the mixture plotted versus the values of the surface areas of the $BiPO_4$ phase corresponding to the "standard" mixture and dispersed–freezed-dried in *n*-pentane catalysts.

Under catalytic reaction conditions, the results (Table 3) show that the sample is slightly reduced even in "standard" conditions for *N*-ethyl formamide dehydration when molecular oxygen is present. If only formamide is present in the reacting medium, the reduction is more pronounced.

It had been shown previously in independent experiments (*5*) that oxygen increased the number of acid sites of the catalyst. The catalytic dehydration of *N*-ethyl formamide needs acid sites (together with basic sites) (*4*).

Our present results are self-consistent with our hypothesis concerning synergy between $BiPO_4$ and $MoO_3$. $BiPO_4$ helps replenish $MoO_3$ with oxygen, when the catalyst is in contact with a gas mixture containing molecular oxygen, thus increasing the number of acid sites, and catalytic activity. The reducing action of *N*-ethyl formamide tends to reduce the number of catalytic sites (we have shown previously that, in the absence of oxygen, the catalyst is much less active, and becomes black, presumably because of reduction and/or carbon deposition (*1, 9*)).

The activity of the catalyst is thus the result of antagonistic dynamic processes: reduction by *N*-ethyl formamide, and reoxidation by oxygen. The essential role of $BiPO_4$ is more easily interpreted by the formation, on this latter phase, of a mobile and very reactive oxygen species. It is this species which reoxidizes the surface of $MoO_3$. This mechanism exactly corresponds to the remote control concept. The "controlling" phase, $BiPO_4$, emits a mobile species, spillover oxygen, which, by reaction with the surface of the "controlled" phase, creates, or regenerates, the active sites.

The present results do not give much information concerning the possible structure of the thus regenerated active sites. They seem to be associated with surfaces containing essentially Mo(VI).

## CONCLUSIONS

The ESR results presented in this paper show the existence of a mutual interaction between $MoO_3$ and $BiPO_4$ phases for reactivity toward reduction. The normalized intensity of the signal of Mo(V) species, used as a monitor of the state of reduction of $MoO_3$–$BiPO_4$ mixture was shown to be strongly dependent of the intimacy of contact between the particles of both phases. Reducibilities of mechanical mixtures are higher than these obtained for single phases. They vary with the mixing method; the method using dispersion of the powders in a liquid being more effective. Still, the synergy between the phases is more efficient in catalyst prepared by coprecipitation.

The reactivity of mechanical mixtures is similar under vacuum or in $H_2$ atmosphere. Alternate reducing and oxidizing treatments show the reaction to be reversible at high temperature.

When considering the relationship between the present results and catalytic activity, one concludes that reoxidation of the surface of $MoO_3$, presumably by spill-over oxygen coming from $BiPO_4$, is necessary to counterbalance the reducing effect of *N*-ethyl formamide, a reduced surface having a lower catalytic activity.

## ACKNOWLEDGMENTS

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