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Catalytic Cooperation between MoO_3 and Sb_2O_4 in N-Ethyl Formamide Dehydration

III. Comparison of a Mathematical Model Based on the Remote Control Mechanism with Experimental Results

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We present a mathematical model of the remote control effect in the cooperation between α-Sb_2O_4 (spillover oxygen donor) and MoO_3 (acceptor and catalytic phase) in the oxygen assisted dehydration of formamides. The model is compared with experimental results obtained with 21 mechanical mixtures of α-Sb_2O_4 and MoO_3 of different compositions, at 3 different reaction temperatures, and oxygen partial pressure varying over a range of more than 2 orders of magnitude. The observed increase of activity of MoO_3 due to the effect of the remote control corresponds extremely well (variance of squared residue better than 3×10^{-3}) to the results of the mathematical model. We have verified that the magnitude of the kinetic parameters and surface concentration of spillover oxygen is physically acceptable, and that the variations of these parameters with the temperature correspond to those predicted by the general laws of physical chemistry.

INTRODUCTION

Multiphase catalysts play an important role in industrial selective oxidation. Among the phases present in these catalysts, molybdenum and antimony oxides occupy a very important place (*1–4*).

We have shown in Louvain-la-Neuve that a large proportion of the two-phase catalysts which are active and selective in allylic oxidation presented a considerable activity in the dehydration of formamides to nitriles (*5–10*). It was found that a small amount of oxygen O_2 should be present in order for these catalysts to maintain their activity and selectivity in dehydration, although O_2 does not take part in the reaction (*5–8, 11, 12*). In our previous studies we have shown that mechanical mixtures of MoO_3 and α-Sb_2O_4 exhibited a remarkable catalytic synergy.

A synergy, namely, an increase of nitrile yield as compared to the addition of the effects due to the isolated compounds, can in principle be explained by different mechanisms:

(i) Bifunctional catalysis.
(ii) Formation of new active compounds by reaction between the two phases.
(iii) Contamination of one phase by an element of the other one.
(iv) Remote control.

Let us summarize the arguments proving the existence of a remote control (*9, 10*).

Classical bifunctional catalysis can be excluded since the only possible intermediary product (isocyanide), having a very low stability, makes its desorption from one phase

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for subsequent adsorption and further reaction on the other phase an extremely unlikely process (*8, 11, 12*).

No indication of the formation of any Mo–Sb–O compound was found (*9, 13*). This is in agreement with Parmentier *et al.* (*14*) who have shown that the formation of Mo–Sb–O compounds (Sb_2MoO_6) or $Sb_2(MoO_4)_3$) can only take place under severe conditions and that, once formed, these compounds decompose very easily.

Surface contamination should also be ruled out. Teller *et al.* (*15, 16*) have reported that Mo is only marginally soluble in β-Sb_2O_4 (high temperature form) but not in α-Sb_2O_4 (low temperature form). This dissolution of Mo was found to occur only at temperatures higher than 1073 K, and it was accompanied by the transition from the α-Sb_2O_4 to the β-Sb_2O_4 structure. In the preceeding papers, we reported results confirming the absence of surface contamination in fresh and used MoO_3–α-Sb_2O_4 mechanical mixtures, using ion scattering spectroscopy (ISS) (*9, 17*).

It seems, thus, that only a remote control mechanism could operate in the synergetic action of α-Sb_2O_4 and MoO_3. A remote control mechanism (*18–21*) corresponds to the case where a second phase (here α-Sb_2O_4) exerts a control on the activity and selectivity of the first phase (namely, the phase which is capable of carrying active centers, MoO_3). This control is exerted by means of mobile surface species (here spillover oxygen) which are formed on the controlling phase. They are transferred (by surface diffusion) on the surface of the controlled phase, with which they react, and form and/or regenerate active (and selective) sites.

In our previous publications (*9, 10, 13, 22–27*) we attributed both the observed synergy and the beneficial role of oxygen to the cooperation between pure MoO_3 and α-Sb_2O_4 phases via a remote control mechanism. Our aim in the present work is to quantitatively describe the control effect of α-Sb_2O_4 on the activity and selectivity of MoO_3 using a mathematical model which takes into account all the parameters related to the remote control mechanism. This model is adapted to N-ethyl formamide dehydration on mechanical mixtures of MoO_3 and α-Sb_2O_4. The validity of the model will be tested by comparing the theoretical with the experimental results. The composition of the mechanical mixtures, the oxygen partial pressure, and the reaction temperature were all modified in order to study their influence on the synergetic effect. We show that a very satisfactory agreement between theory and results exists. The physicochemical meaning of the kinetic parameters, as well as their variation under the influence of the different experimental parameters, is also discussed.

EXPERIMENTAL

The experimental results concerning the catalytic activity were obtained on a series of 21 mixtures of different compositions. The separately prepared MoO_3 (2 m^2 g^{-1}) and α-Sb_2O_4 (2 m^2 g^{-1}) were mixed using a standard procedure which, along with the catalytic reaction conditions, are detailed elsewhere (*9*). We summarize only briefly the important parameters used in the measurements reported in the present work: an overall quantity of catalyst of 130 mg was used; the contact time t is 11.3 s; the partial pressure of N-ethyl formamide is 6 Torr (1 Torr = 133.3 N m^{-2}) and the partial pressure of oxygen varies from 0.3 to 45 Torr; the reaction is carried out at 350, 370, and 390°C.

Even when alone, MoO_3 presents a modest activity of its own. The remote control effect only modifies the additional (more fragile) catalytic centers that MoO_3 can develop thanks to the action of spillover oxygen. This is schematically represented in Fig. 1. This is a plot of propionitrile yield vs. composition of the mechanical mixtures of α-Sb_2O_4 and MoO_3. We assume that the yield in propionitrile is directly proportional to the number of active sites. This seems justified as long as we keep conversions (practically equal to yields) relatively low,

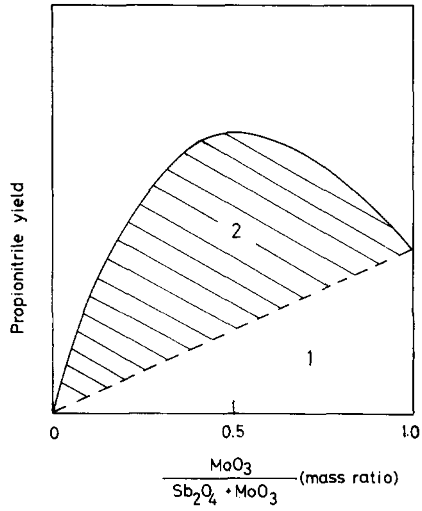

FIG. 1. Dehydration of N-ethyl formamide to propionitrile: activity, expressed as the propionitrile yield, as a function of mass ratio. (1) activity due to the MoO_3 present in the samples, (2) activity due to synergetic effect.

as in the present work. The dashed straight line corresponds to the propionitrile yield which would be achieved with the quantity of MoO_3 contained in the corresponding mixture (e.g., for point 0.5, when 65 mg of MoO_3 is present in the overall 130 mg of catalyst, half the yield produced by 130 mg of pure MoO_3). The hatched surface corresponds to the effect of the remote control (at point 0.5, this corresponds to an additional yield twice as large as the one due to pure MoO_3).

DESCRIPTION OF THE MATHEMATICAL MODEL

The mathematical model developed here corresponds to the application of the remote control mechanism to the case of N-ethyl formamide dehydration. In order to facilitate the mathematical description, will shall call α-Sb_2O_4 (which is able to produce the spillover oxygen) the donor phase (denoted by D), and MoO_3 (onto which the spillover oxygen migrates for producing and regenerating active sites) the acceptor phase (A). The meanings of the symbols are listed at the end of this paper.

The net rate of formation of spillover oxygen on D corresponds to a dynamic balance between the dissociation of molecular oxygen from the gas phase producing spillover oxygen and the recombination of this spillover oxygen. The recombination of spillover oxygen is proportional to the square of the surface concentration of spillover oxygen (proportional to the fraction of surface sites occupied by spillover oxygen $[O]_D$). Dissociation of O_2 molecules to spillover oxygen is proportional to the oxygen partial pressure P_{O_2} and depends on the availability of pairs of vicinal vacant adsorption sites (hence a proportionality to $(1 - [O]_D)^2$). If we calculate the net rate of formation of spillover oxygen (dissociation of O_2 minus recombination) in mol s^{-1} per square meter of donor phase, we have

$$\tau_F = k_d \times P_{O_2} \times (1 - [O]_D)^2 - k_{id} \times [O]_D^2.$$

The above equation is multiplied by S_D (i.e., the surface area developed by the donor phase in 1 g of mixture with composition r, expressed as mass ratio $MoO_3/(MoO_3 + \alpha\text{-}Sb_2O_4)$) to give the net rate of formation of spillover oxygen in mol s^{-1} per gram of mixture,

$$R_F = k_d \times P_{O_2} \times (1 - [O]_D)^2 \times S_D - k_{id} \times [O]_D^2 \times S_D. \quad (1)$$

The rate of migration of spillover oxygen from the donor to the acceptor phase is assumed to be proportional to the difference between the oxygen surface concentrations or, more precisely, the fractions of potential adsorption sites occupied on phase D and phase A,

$$R_T = k_t \times F_t \times ([O]_D - [O]_A). \quad (2)$$

On the acceptor phase, at the steady state, the rate of consumption of spillover oxygen corresponds to its reaction with the inactive MoO_3 surface (fraction: $1\text{-}\alpha$) for producing the active sites. This rate represents the rate (τ_t) at which new sites are created (in mol sec^{-1} per square meter of acceptor phase),

$$\tau_t = k_a \times a \times (1 - \alpha) \times [O]_A.$$

This equation is multiplied by S_A (i.e., the surface area developed by the acceptor phase in 1 g of mixture with composition r) to give the rate of consumption of spillover oxygen (or of production of new active sites) in mol sec^{-1} per gram of mixture,

$$R_t = k_a \times a \times (1 - \alpha) \times [O]_A \times S_A. \quad (3)$$

The destruction of the active sites is linked to the catalytic process. There exists a certain probability (small) that the reaction of a formamide molecule goes wrong and the catalytic center gets deactivated. The rate of destruction of the active sites is thus proportional to the turnover rate. This in turn depends on (is proportional to) the reactant partial pressure. Let us represent this partial pressure by f. The rate of destruction of the active sites, in mol sec^{-1} per gram of mixture is given by

$$R_r = k_{ia} \times a \times \alpha \times f \times S_A \quad (4)$$

At the steady state, the rates of oxygen spillover formation, transfer, and loss, are all equal,

$$R_F = R_T = R_t. \quad (5)$$

At the steady state, the number of sites activated per unit time is equal to the number of sites destroyed,

$$R_t = R_r. \quad (6)$$

We define the following parameters:

$$A = k_{ia}/k_a \quad (7)$$

$$B = k_d/k_{id} \quad (8)$$

$$C = a \times k_{ia}/k_{id} \quad (9)$$

$$D = a \times k_{ia}/k_t Q_t \quad (10)$$

$$E = a \times k_{ia}. \quad (11)$$

From Eqs. (1), (4), (5), and (6), we get

$$[O]_D = \frac{-B \times P_{O_2} + \{(B \times P_{O_2})^2 + (1 - B \times P_{O_2}) \times (B \times P_{O_2} - C \times \alpha \times f \times S_A/S_D)\}^{1/2}}{1 - B \times P_{O_2}}. \quad (12)$$

From Eqs. (2)–(6), it is found that the fraction of surface sites occupied by oxygen spillover on the donor phase may be given also from the following equation:

$$[O]_D = A \times f \times \alpha/(1 - \alpha) + D \times f \times \alpha/S_D. \quad (13)$$

Finally, from Eqs. (3), (4), and (6), the following equation giving the fraction of surface sites occupied by spillover oxygen on the acceptor phase is derived:

$$[O]_A = A \times \alpha \times f/(1 - \alpha). \quad (14)$$

From Eqs. (12) and (13) the value of a is found (for a given set of the parameters A, B, C, and D) using an iteration method under the following constraints:

$$0 < \alpha < 1 \quad \text{and} \quad [O]_D > 0.$$

The procedure of iteration continues until the difference ($[O]_D$ deduced from Eq. (12) − $[O]_D$ deduced from Eq. (13)) becomes less than a predetermined value, which had been chosen to be equal to $10^{-6}/([O]_D$ deduced from Eq. (12)). For a set of parameters, A, B, C, and D, the value of α was calculated for each experimental point. From Eq. (4) it comes that

$$R_r = -df/dt = k_{ia} \times a \times \alpha \times f \times S_A.$$

From the above equation we get

$$X = 1 - \exp(-E \times \alpha \times S_A \times t). \quad (15)$$

Parameter E was calculated from Eq. (15) by linear regression.

The optimum values of the parameters A, B, C, and D (that we define as those which minimize the function $\Sigma(X_{exp.} - X_{theo.})^2/n$) have been found using a nonlinear optimization program (*28*).

RESULTS

For each reaction temperature the mathematical model led after optimization to a set of parameters A, B, C, D, and E. Taking into account the definitions of these parameters (Eqs. (7)–(11)) we calculated the kinetic constants of the model which are presented

TABLE 1

Optimal Parameters, Kinetic Constants, and Variance of Squared Residue for 350, 370, and 390°C

Parameters	350°C	370°C	390°C
A (×10^{-4})	2.53	1.00	1.34
B	2.96	99.92	283.90
C	1.09	29.78	76.16
D	0.61	0.91	0.97
E	0.29	0.94	1.45
$a \times k_{ia}$	0.294	0.942	1.452
$a \times k_a$	1164	9420	10836
k_{id} (×10^{-1})	2.70	0.32	0.19
k_d	0.798	3.162	5.418
$k_t \times Q_t$	0.486	1.038	1.500
$\frac{\Sigma(X_{exp.} - X_{theo.})^2}{n}$ (×10^{-3})	0.87	0.30	2.28

in Table 1, along with the optimum values of the parameters and the variance of the squared residue of all points at the same temperature.

We observe that, with the increase of temperature, the rate constant corresponding to the creation of active sites (k_a) and that of formation of spillover oxygen (k_d) increase remarkably. The rate constant of destruction of spillover oxygen (k_{id}) decreases, whereas the other constants (k_{ia}, $k_t \times Q_t$) increase only slightly.

The theoretical curves calculated with these kinetic constants for different compositions of the mechanical mixtures, oxygen partial pressures, and reaction temperatures are presented in Figs. 2–5, along with the experimental points determined under the same conditions. In all cases the experimental points are strikingly close to the theoretical curves. In Fig. 2 we presented both the contributions of the remote control alone (bottom curve and experimental points) and the total effect, account taken of the activity of pure MoO_3 (see Fig. 2). The effect of remote control alone is shown in Figs. 3, 4, and 5.

Table 2 presents the theoretical values of $[O]_D$, $[O]_A$, and α for different sample compositions at 370°C and oxygen partial pressure equal to 3 Torr. For all samples, the fraction of surface sites occupied by spillover oxygen on the donor phase ($[O]_D$) is always about four orders of magnitude

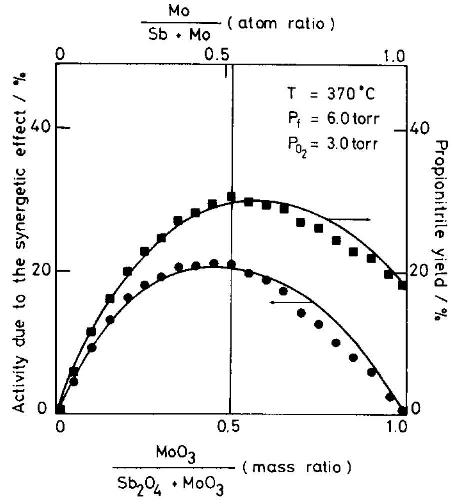

FIG. 2. Comparison of theoretical calculations (curves) and experimental results (points) under reaction conditions T = 370°C, P_f = 6.0 Torr, and P_{O_2} = 3.0 Torr. Upper curve: total yield. Lower curve: increment of yield with reference to nonpromoted MoO_3, due to remote control.

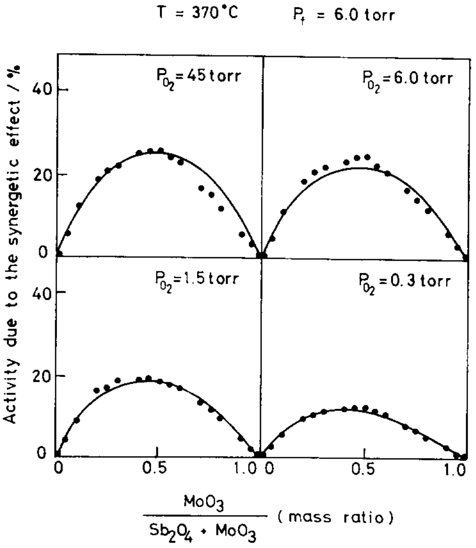

FIG. 3. Comparison of theoretical calculations (curves) and experimental results (points) under reaction conditions 370°C, P_f = 6.0 Torr, and P_{O_2} = 45, 6.0, 1.5, and 0.3 Torr.

higher than the corresponding fraction on the acceptor phase ($[O]_A$). The fraction of surface sites occupied by spillover oxygen decreases, in both the donor and acceptor phases, with the increase of the mass ratio r; that is both these fractions decrease as the MoO_3 content increases in the samples. The fraction of active sites on the surface of the acceptor phase (α) shows a variation similar to that of $[O]_D$ and $[O]_A$, i.e., it decreases with the increase of the MoO_3 content in the samples.

The variation of the theoretical values of $[O]_D$, $[O]_A$, and α with the oxygen partial pressure (for the same sample, $r = 0.5$) at 370°C is depicted in Fig. 6. The fraction of surface sites occupied by spillover oxygen on both donor and acceptor phases, as well as the fraction of active sites on MoO_3, increases with the oxygen partial pressure from 0.3 to 6 Torr. Further increase of oxygen pressure from 6 to 45 Torr does not bring about any important increase of the surface concentrations of spillover oxygen or active sites. The variation of the experimental activity with the oxygen partial pressure is also presented in the same figure. There exists a striking parallelism between the theoretical curves ($[O]_D$, $[O]_A$, and especially α, the fraction of activated sites) and the experimental results (propionitrile yield).

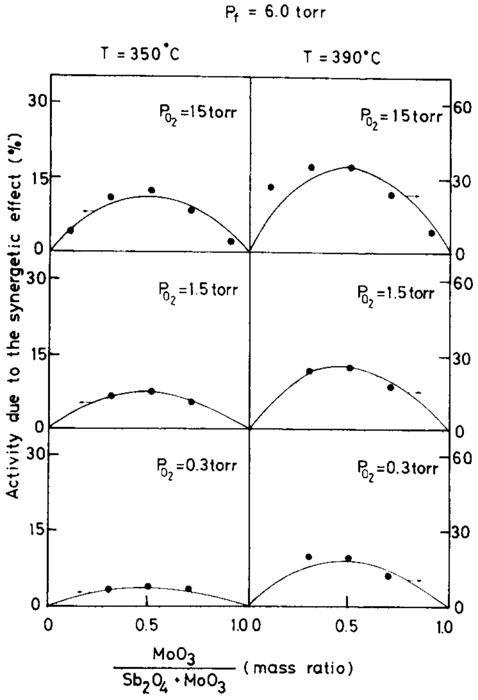

FIG. 5. Comparison of theoretical calculations (curves) and experimental results (points) under reaction conditions 350 and 390°C, with $P_f = 6.0$ Torr, and $P_{O_2} = 15$, 1.5, and 0.3 Torr.

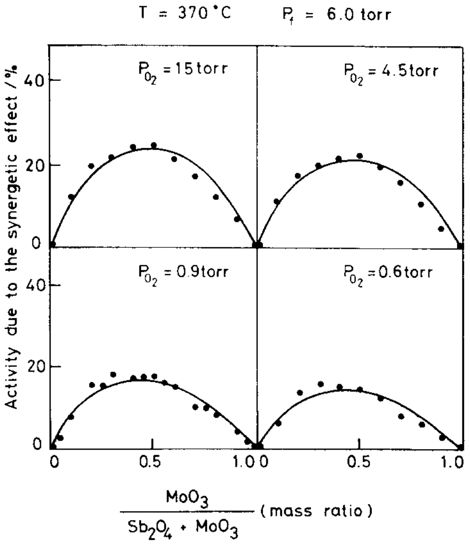

FIG. 4. Comparison of theoretical calculations (curves) and experimental results (points) under reaction conditions 370°C, $P_f = 6.0$ Torr, and $P_{O_2} = 15$, 4.5, 0.9, and 0.6 Torr.

DISCUSSION

The proposed mathematical model, based on the principles of the remote control mechanism, provides a quantitative representation of the effects of oxygen partial pressure and the reaction temperature on the synergy exhibited by MoO_3-α-Sb_2O_4 mechanical mixtures in the dehydration of N-ethyl formamide. In all cases the experimental points agree in a strikingly satisfactory way with the theoretical curves. Particularly remarkable is the fact that this agreement is observed for oxygen pressures varying by more than two orders of magnitude.

TABLE 2

Theoretical Values of $[O]_D$, $[O]_A$, and α for Different Sample Compositions at 370°C, $P_f = 6.0$ Torr, and $P_{O_2} = 3.0$ Torr

r	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$[O]_D$	0.855	0.807	0.771	0.742	0.717	0.695	0.676	0.659	0.643
$[O]_A (\times 10^{-4})$	2.36	1.86	1.48	1.17	0.909	0.682	0.482	0.305	0.145
α	0.282	0.234	0.198	0.163	0.132	0.102	0.074	0.048	0.024

However, a model, whatever the quality of agreement with the experimental results, must always be examined in a very critical way. The parameters (rate constants, fraction of active sites, etc.) and the quantities corresponding to nonmeasurable species ($[O]_D$ and $[O]_A$) must have reasonable values and vary in a way consistent with the laws of physical chemistry. This critical examination will be focused on the following three aspects: (i) kinetic parameters, (ii) fractions of surface sites occupied by spillover oxygen, and (iii) fraction of the active sites.

Kinetic Parameters

The influence of the temperature can be observed from the data given in Table 1. As the temperature increases the rate constant of the dissociation of oxygen (k_d) increases remarkably, whereas the rate constant of the recombination of oxygen (k_{id}) decreases. These variations are consistent with the ki-

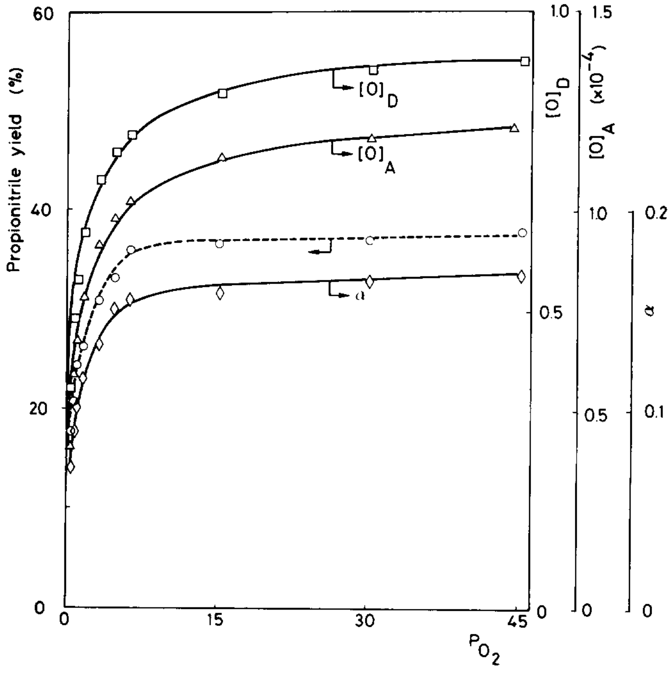

FIG. 6. Theoretical values of $[O]_D$, $[O]_A$, and α as a function of partial oxygen pressure in comparison with activity (expressed as the propionitrile yield) results (dashed curve) obtained at 370°C and P_f = 6.0 Torr with the sample $r = 0.5$.

netic and thermodynamic laws. Indeed, with the increase of temperature, the vibration of the bond associating the two oxygen atoms becomes more and more intense; this facilitates the dissociation of the molecular oxygen into two spillover oxygens. The recombination of the spillover species probably necessitates little or no activation energy: whatever the formal charges carried by the spillover species (unknown), the latter are essentially adsorbed atoms, which could recombine easily. Thus, the only factor which could influence the recombination rate is the entropy-dependent factor (concentration of the transient state association between two spillover species). This factor obviously decreases with increasing temperature.

The rate constants of the creation and of the destruction of active sites, k_a and k_{ia}, must both increase with the temperature; this is indeed the case. We should note, however, that k_a, the constant corresponding to the control effect, increases by a factor of 10, whereas k_{ia} increases only by a factor of 5, when the reaction temperature increases from 350 to 390°C. This implies that the remote control effect plays a more important role at high temperature. We had already observed (*29*) that formamide dehydration with two phase catalysts (MoO_3 + Sb_2O_4, as in the present case) had surprisingly a higher selectivity at higher temperatures. We had attributed this fact to the higher proportion of O^{-2} species (the useful spillover species) flowing into the surface of MoO_3. The parameter $k_t \times Q_t$, which determines the transfer of spillover oxygen, increases only by a factor of 3 with the temperature changing from 350 to 390°C. This is probably due to the fact that the diffusion of the spillover oxygen has a relatively low activation energy.

As a conclusion, both the physico-chemical significance of the kinetic parameters and their changes under the different reaction conditions is logical.

Fractions of Surface Sites Occupied by Spillover Oxygen

The values of $[O]_D$ and $[O]_A$ in Table 2 and Fig. 6 are consistent with the model, namely, $[O]_D$ is higher than $[O]_A$ (a flux of [O] can take place from D to A) and both fractions are higher when the quantity of D is higher. Both decrease when the mass ratio (r) increases (as expected, if there is less donor phase to supply oxygen spillover).

An unexpected, although not really surprising conclusion of the mathematical analysis is that $[O]_D$ is so much higher than $[O]_A$ (about 4 orders of magnitude). The explanation lies in the fact that the surface diffusion is slow and the transfer from the donor to the acceptor phase probably difficult. These aspects have already been considered when spillover phenomena were mentioned. For the hydrogen spillover, many authors have deduced, or assumed, that the surface diffusion is the rate-determining step (*30–33*). Especially, Cavanagh and Yates have postulated that the migration of spillover hydrogen on the surface is slow (*33*). In a more recent study, Cevallos-Candau and Conner concluded that the transfer of spillover hydrogen from the source of spillover onto the accepting surface is difficult (*34*).

When considering the influence of oxygen pressure on $[O]_D$ and $[O]_A$ (Fig. 6) a striking feature is the existence of a saturation effect. An oxygen pressure of 6 Torr suffices for reaching the high occupancy of the donor sites by spillover oxygen, and a further increase of the pressure from 6 to 45 Torr does not bring about any important augmentation of $[O]_D$ and $[O]_A$.

This mathematical analysis suggests that, with very large particles as in our samples (specific surface area of 2 $m^2\ g^{-1}$) and presumably relatively poor contacts, the flow of spillover oxygen from D to A is quite difficult. Delmon and Ruiz, in an approximate calculation, have shown that the quantity of transferred spillover species could be multiplied by a factor as high as 10^4, if the size of the particles were divided by a factor of only 10 (*35*). The present mathematical analysis, together with this evaluation, opens prospects for quite important effects if more numerous contacts are created and made more effective.

Fraction of the Active Sites

The change of α with the sample composition reported in Table 2 is reasonable in view of the remote control mechanism. The similitude between $[O]_A$ and α indeed shows directly the quantitative influence of the spillover oxygen on the fraction of the active sites.

This conclusion is further confirmed by the results presented in Fig. 6. These results were obtained for the same sample with the composition $r = 0.5$. In this case, the maximum density of active sites is always the same. Under these conditions, we can compare directly the activity with the fraction of the active sites. The striking parallelism between the experimental results (propionitrile yield) and the theoretical values of α demonstrates further the validity of the mathematical model.

CONCLUSIONS

The mathematical model corresponding to the remote control mechanism describes very satisfactorily the experimental results and gives a quantitative explanation of the results. The variations of the kinetic parameters used in the mathematical model are consistent with the general laws of physical chemistry. This excellent agreement constitutes a further strong evidence of the intervention of a remote control in the oxygen aided dehydration of formamides.

APPENDIX: SYMBOLS

α	Fraction of the active sites on the surface of the acceptor phase at steady state.
a	Maximum density of active sites on the surface of acceptor phase.
f	Final partial pressure of N-ethyl formamide (Torr).
k_a	Rate constant of the creation of active sites on the surface of the acceptor phase.
k_{ia}	Rate constant of the destruction of the active sites during the reaction on the surface of the acceptor phase.
k_d	Rate constant for the formation of spillover oxygen (dissociation of molecular oxygen into two mobile oxygen species) on the surface of the donor phase.
k_{id}	Rate constant for the destruction of spillover oxygen (recombination of the two mobile oxygen species into molecular oxygen) on the surface of the donor phase.
k_t	Rate constant for the transfer of spillover oxygen from the donor onto the acceptor phase.
r	Mass ratio; $r = MoO_3/(MoO_3 + \alpha\text{-}Sb_2O_4)$.
t	Contact time (sec).
x	Conversion of N-ethylformamide to propionitrile (%).
A	Acceptor phase.
D	Donor phase.
F_t	Contact factor (efficiency of contact with respect to the jump of oxygen from D to A; $F_t = Q_t \times S_D \times S_A$).
$[O]_A$	Fraction of surface sites occupied by spillover oxygen on the acceptor phase.
$[O]_D$	Fraction of surface sites occupied by spillover oxygen on the donor phase.
P_{O_2}	Partial pressure of oxygen (Torr).
Q_t	Contact quality depending on the procedure of mixture; it is considered to be constant when the same procedure is used for mixing A and D.
R_F	Net rate of formation of spillover oxygen (mol sec^{-1} per gram of mixture).
R_t	Rate of loss of spillover oxygen (mol sec^{-1} per gram of mixture).
R_r	Rate of destruction of active site (mol sec^{-1} per gram of mixture).
R_T	Rate of migration of spillover oxygen (mol sec^{-1} per gram of mixture).

S_A Surface area developed by the acceptor phase in 1 gram of mixture with composition r (m^2 g^{-1}).
$S_A = r \times \sigma_A$, where σ_A is the specific surface area of the acceptor phase.

S_D Surface area developed by the donor phase in 1 gram of mixture with composition r (m^2 g^{-1}).
$S_D = (1 - r) \times \sigma_D$, where σ_D is the specific surface area of the donor phase.

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