Synergy in N-Ethylformamide Dehydration by Mixtures of MoO₃ and α -Sb₂O₄

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Mixtures of separately prepared MoO₃ and α -Sb₂O₄ show a remarkable synergy in the dehydration of N-ethylformamide to propionitrile when a small amount of oxygen is fed together with the main reagent. The surface acidity of the samples was investigated by TPD of ammonia. ESR and XPS were used for investigating the behavior of the mixtures in reducing and oxidizing conditions. The acidity is attributed mainly to Brønsted sites situated on MoO3. Oxygen is necessary to maintain these sites. The interpretation is that oxygen is provided, to the surface of MoO_3 , in the form of spillover oxygen, by α -Sb₂O₄. Such a mechanism corresponds to what has been called a remote control.

Introduction

The dehydration of formamides to nitriles takes place on a family of catalysts known to be also active in selective oxidation (P-Bi-Mo, MoO₃ + Bi₂O₃, MoO₃ + α -Sb₂O₄, etc.); on those catalysts, it is necessary that a small amount of oxygen O₂ ("dioxygen"), be present in order for the catalysts to be selective and not to deactivate.¹⁻⁴ A synergy, namely, an increase of nitrile yield compared to the addition of the effects due to the isolated compounds, exists; even in simple mechanical mixtures of separately prepared oxides, a strong synergetic effect was observed.^{3,4}

The synergy and the positive effect of dioxygen were explained by the formation, or regeneration, of active sites on one of the phases (supposed to be MO_3), thanks to the action of a mobile species (spillover oxygen) flowing from the other phase. This constituted an embodiment of the remote control concept, 5-8 which proposes that in certain cases a second phase (here α -Sb₂O₄) exerts a control of the activity of the first phase (MoO_3) . More precisely, the concept supposes that the presence of this second phase brings about a change in the number of active sites of the first or controlled phase. The "messenger" carrying this information is a surface species (here spillover oxygen) sent by the controlling phase.5

The dehydration of formamides to nitriles is conceptually a very good example for studying a synergy between separate phases, because classical bifunctional catalysis can be ruled out on the basis of the very low stability of the only possible intermediary product, namely, an isocyanide, the desorption of which from one phase, for adsorption and further reaction on the other phase, seems extremely unlikely.⁴ Our previous studies have shown that the selectivity of transformation of N-ethylformamide to propionitrile was, together with the overall conversion, an indication of the magnitude of synergy.

On the other hand, a previous study³ had shown that a standard mixture of MoO₃ and α -Sb₂O₄ constituted an ideal catalytic system, because isolated α -Sb₂O₄ gave a negligible yield in propionitrile. This result supported the hypothesis that MoO₃ was the controlled phase and carried the centers active in dehydration and suggested that the roles of the controlling $(\alpha - Sb_2O_4)$ and controlled phase could be clearly separated.

The aim of the present work is to further study the interaction between α -Sb₂O₄ and MoO₃ and to explore in more detail the role of oxygen.

In a general way, synergy between two phases can be explained by different mechanisms: bifunctional catalysis, formation of new compounds by reaction between those phases, contamination of one phase by an element of the other one, and remote control.⁵⁻⁸ As indicated above, bifunctional catalysis is excluded in the present case. But formation of new compounds and contamination should be considered. There are no indications of formation of any Mo-Sb-O compound in our samples (X-ray diffraction, electron

spin resonance spectroscopy (ESR)). This is logical as the work of Parmentier et al. has shown that the formation of Mo-Sb-O compounds only took place in very severe conditions and that, when formed, these compounds decomposed very easily.9 Surface contamination is ruled out by careful ISS measurements.¹⁰ On the other hand, Teller et al. have postulated that Mo is marginally soluble in β -Sb₂O₄ (high-temperature form) but not in α -Sb₂O₄ (low-temperature form). This dissolution of Mo only occurs at a temperature higher than 1073 K and with concurrent transition from α -Sb₂O₄ to β -Sb₂O₄.^{11,12} We are thus led to consider that a remote control mechanism does operate in the synergetic action of α -Sb₂O₄ and MoO₃.

If a remote control operates, namely, a mobile species is formed on the surface of one phase and modifies the active sites on the other, the parameters of relevance should be the surface areas rather than the weights of the oxides. With $MoO_3 + BiPO_4$ standard mixtures, earlier studies⁴ indeed had shown that maximum synergy was obtained when the total surface area developed by one phase was comparable to that of the other phase. When samples of different specific surface areas were used, the position of maximum activity, expressed in mass ratio, changed to the values where the surface areas developed by the quantities of oxides in contact were again comparable. The mobility of oxygen and the interaction with MoO₃ that the remote control supposes should, in principle, have consequences other than just a modification of the active sites. It could, in particular, be involved in transformations of solids. With the P-Bi-Mo system, an enhancement of the rate of reduction of MoO_3 in the presence of BiPO₄ was indeed observed.⁴ It was explained by a spillover of oxygen from MoO_3 to BiPO₄, from where it escaped (reverse spillover). We investigated whether the same effect takes place in the MoO_3 + α -Sb₂O₄ system.

On the other hand, if we accept that a remote control mechanism is operative, we should try to identify the active centers which are created or regenerated by the oxygen mobile species. Experiments with another test reaction, the dehydration of 4methylpentan-2-ol, had shown, with the P-Bi-Mo system, that

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the presence of dioxygen strongly increased the number of acid sites.¹ For that, we also conducted NH₃ temperature-programmed desorption (TPD) experiments in the present study to investigate whether the same effect arises in the MoO₃ + α -Sb₂O₄ system.

Experimental Section

Materials. The products used as starting materials for sample preparation were ammonium heptamolybdate $((NH_4)_6Mo_7-O_{24}\cdot4H_2O)$ and antimony(III) oxide $(Sb_2O_3, Merck, p.a.)$.

The reactant for catalytic activity experiments was N-ethylformamide (>99%) from Fluka. For calibration of the GC column, propionitrile (99%) and acetonitrile (99%), Merck, were used.

Gases were from l'Air Liquide Belge: He (99.995%); O_2 (99.995%) + He (99.995%) in a cylinder containing a mixture composed of 10.0% O_2 and 90.0% He. They were used without further purification.

Ammonia was from Matheson: ammonia, anhydrous (> 99.96%).

Catalyst Preparation and Characterization. Pure MoO₃ and α -Sb₂O₄ powders were prepared as follows: MoO₃ (2 m²·g⁻¹) by thermal decomposition of ammonium heptamolybdate in air at 773 K for 20 h and α -Sb₂O₄ (2 m²·g⁻¹) by calcination of Sb₂O₃ in air at 773 K for 20 h.

Standard mixtures of MoO₃ and α -Sb₂O₄ were obtained by vigorously mixing the suspension of solids in *n*-pentane by means of a mixer (Ultra-Turrax from Janke and Kunkel) followed by evaporation under stirring at a pressure lower than 0.1 MPa. Remaining *n*-pentane was removed by drying in air at 343 K for 20 h.

Powder mixtures of composition $r = MoO_3/(MoO_3 + \alpha - Sb_2O_4)$ (mass ratio) varying from r = 0 to 1.0 were prepared.

BET surface areas were measured gravimetrically with a Setaram MTB 10-8 microbalance by N_2 adsorption at 77 K.

Crystal structure were characterized by X-ray diffraction (Kristalloflex 805 Siemens diffractometer, Ni-filtered Cu K α radiation).

X-ray photoelectron spectroscopy (XPS) spectra were taken in a Vacuum Generator ESCA-3 Mk II spectrometer; the exciting radiation was Mg K α (1253.6 eV). All three samples were introduced into the apparatus at the same time, thus ensuring that the contamination by carbon coming from the apparatus was the same. The recording sequence was also maintained identical in order to avoid spurious effects due to the progressive contamination of each sample during the course of analysis. Total accumulation time was about 3 h. The C 1s, Sb $3d_{5/2}$ + O 1s, Sb $3d_{3/2}$, Mo 3d, and O 2s lines were swept successively. The C 1s line of carbon was used as reference (binding energy 285 eV). Concentrations (I) were calculated from XPS intensities by using "atomic sensitivity factors" given by Wagner et al.¹³

Ion scattering spectroscopy (ISS) was also used in this work. Let us recall that, in ISS, the surface of the samples is bombarded by ions (here ²⁰Ne⁺) which suffer elastic scattering when colliding with the top surface atoms. The energy of the scattered ions is characteristic of the surface atoms (here Mo or Sb). The ratio of signal intensities corresponding to Mo and Sb (I_{Mo}/I_{Sb}) reflects the average composition of the surface of the whole sample.

The ISS measurements were carried out with a Kratos spectrometer (Wg 541-515) in which a CMA energy analyzer is mounted coaxially with the ion gun. The samples were bombarded at normal incidence. The ions, backscattered in a conical solid angle of 138° with respect to the primary beam direction, were detected and analyzed. The energy resolution $\Delta E/E$ of the analyzer is 3%. A beam of Ne ions with an energy of 2 keV corresponding to a total current of 10 nA was used and rastered on a square area of $1 \times 1 \text{ mm}^2$.

Catalytic Activity Measurements. Catalytic activities were measured in a conventional flow apparatus. The reactor was made of stainless steel (i.d. 5 mm). All connections (stainless steel) were heated to avoid condensation of formamide or nitrile. The catalytic bed (0.13 g) was maintained between two layers of quartz wool. The reaction was studied at 623, 633, and 648 K.

N-Ethylformamide was fed by saturation of a carrier gas passing through a saturator placed in a thermostated bath held at 363 K. The carrier gas was the wanted mixture of helium and oxygen. The total gas hourly space velocity was $40\,000 \ h^{-1}$. The liquid hourly space velocity was estimated to be 1.7 h^{-1} .

Products of reaction were anayzed by "on line" gas chromatography (Intersmat IGC 120 ML) with a Poropak Q column (2 m, 473 K).

Reaction products were propionitrile, acetonitrile, water, and CO_2 :

$$C_{2}H_{5}-NH-C$$
 H $cat.$ $C_{2}H_{5}-C\equiv N + H_{2}O$ (1)
 $+(3/2)O_{2}$ $CH_{3}-C\equiv N + 2H_{2}O + CO_{2}$

Propionitrile formation is the main reaction.

Catalytic activities were expressed as yields (Y, %), namely, percentage of propionitrile in the mixture (propionitrile + acetonitrile + unreacted N-ethylformamide). Selectivities (S, %) were calculated from the equation S = Y/C, where conversion (C, %)was the total percentage of formamide transformed. The reproducibility in the measurements of conversion was $\pm 1\%$.

Temperature-Programmed Desorption of Ammonia. TPD curves of desorbed ammonia were obtained with a versatile apparatus with a thermal conductivity detector. Two series of measurements were made. In a first series, a sample of ca. 0.2 g was preheated under argon at 723 K for 1 h, exposed to ammonia at 298 K for 30 min, and flushed at that temperature with helium for 30 min. TPD measurements were carried out from that temperature up to 723 K under a flow of helium, with a heating rate of 10 K·min⁻¹. The amount of ammonia which desorbed (in micromoles of NH₃ per gram of sample) during those TPD runs is assumed to correspond to the total surface acidity of studied samples.

In the second series of measurements, ca. 0.2 g of a standard mixture of composition r = 0.5 was reduced with H₂ at 423 K for 1 h, flushed with helium at 298 K, and exposed to NH₃ as before. The TPD run was carried out from 298 up to 633 K. The sample was then reoxidized with O₂ (10% of O₂ in He) at 423 K for 1 h, and the whole procedure was repeated.

The quantity of ammonia adsorbed by the samples was estimated by a calibration method, namely, by comparison with the integral thermal conductivity signals obtained with exactly known amounts of NH_3 .

ESR Measurements (Reduction of Mo^{6+} to Mo^{5+}). ESR measurements were carried out in the X-band Varian E-12 spectrometer with double cavity. The frequency of modulation was 100 kHz. The power of the incident microwave beam was about 20 mW.

The sample holder, made of pure quartz, was connected to a vacuum and gas handling system. In order to avoid contamination of the samples by vacuum grease, a liquid nitrogen trap was used just before the entrance to the sample holder. The reduction of the samples was made by hydrogen (0.067 MPa) in the temperature range of 423-723 K.

Some cycles were conducted at 423 K in a succession of reducing and oxidizing conditions. For that, heating in hydrogen was stopped at 423 K for 1 h and followed by exposure to air at 298 and 423 K for 1 h. Experiments were performed also at 523 K without exposure to air.

The relative quantity of Mo^{5+} in samples was calculated from the following equation

$$(Mo^{5+})_{rel} = \frac{I\Delta H^2}{I_0} \frac{S_s}{S} \frac{1}{m} \frac{1}{r}$$
(2)

where I is the intensity of the signal characteristic for Mo^{5+} , ΔH is the width of the signal for Mo^{5+} , I_0 is the intensity of the internal

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Figure 1. XPS peaks of $\text{Sb3d}_{3/2}$ and Mo3d in the MoO₃ + α -Sb₂O₄ standard mixtures: I, I', before the catalytic test; II, II', after the catalytic test in the presence of oxygen; III, III', after the catalytic test in the absence of oxygen.

TABLE	I:	XPS	Concentration	Ratios ⁴

samples	$rac{I_{\mathrm{Sb}\ \mathrm{3d}_{\mathrm{3/2}}}}{\sum I}/$	$I_{Mo 3d} / \sum_{I}$	$I_{{ m Sb}~3{ m d}_{3/2}}/I_{{ m C}~1{ m s}}$	$rac{I_{ m Mo~3d}}{I_{ m C~1s}}/$
standard mixture $(r = 0.5)$ before catalytic reaction	0.258	0.742	0.262	0.751
standard mixture ($r = 0.5$) after catalytic reaction in the presence of O ₂	0.273	0.727	0.272	0.724
standard mixture ($r = 0.5$) after catalytic reaction in the absence of O_2	0.435	0.565	0.200	0.260
$a \sum I = I_{\text{Sb } 3d_{3/2}} + I_{\text{Mo } 3d}$				

standard (pitch), S is the selected sensitivity of the apparatus during measurement, $S_s = 1.25 \times 10^4$ (standard sensitivity), m is the mass of the samples (g), and r is the mass ratio. The quantity of Mo⁵⁺ ions is expressed in relation to the amount of MoO₃ in the studied catalysts.

Results

A. Characterization. 1. Surface Area. The cosuspension of the pure oxides in *n*-pentane did not bring about any noticeable modification of the BET surface area, which remained of $2 \text{ m}^2 \text{ g}^{-1}$.

2. X-ray Diffraction. The X-ray diffraction spectra of the pure oxide showed the lines characteristic for the corresponding orthorhombic phases. These lines do not change after a catalytic test. Dispersing the oxides in *n*-pentane did not modify the phases. The X-ray diffraction patterns of the standard mixtures correspond exactly to the addition of those corresponding to the pure oxides. 3. X-ray Photoelectron Spectroscopy (XPS). The results of

XPS measurements are presented in Figure 1 and Table I.

The values of binding energy (Be) and intensity of the Sb $3d_{3/2}$ and Mo 3d lines were practically identical for the standard mixtures (r = 0.5) before and after tests in the dehydration of *N*-ethylformamide in the presence of oxygen. The BE at 540.8 eV was attributed to Sb $3d_{3/2}$ electrons in α -Sb₂O₄,¹⁴ and those at 236.0 and 233.0 eV were due to Mo $3d_{3/2}$ and Mo $3d_{5/2}$ in MoO₃, respectively,¹⁵ (Figure 1, curves I, I', II, II').

After 8 h on stream in the absence of oxygen, there were indications of slight superficial reduction of both oxides. The BE of Sb $3d_{3/2}$ changed from 540.8 to 540.2 eV (Figure 1, curve III). For molybdenum, a certain contribution of Mo⁴⁺ and possibly

TABLE II: ISS Results



Figure 2. Synergy curves for $MoO_3 + \alpha$ -Sb₂O₄ standard mixtures at 623 (O), 633 (\bullet), and 648 K (\Box).

Mo^{5+15,16} must exist, because a superposition of the bands at 232.8 eV and a shoulder band at about 229.9 eV were observed (Figure 1, curve III'). In addition, the intensity of Mo 3d decreased relatively to that of Sb $3d_{3/2}$ when comparing the results for standard mixtures before and after the reaction in the absence of oxygen (Table I).

Another observation was that (again after 8 h on stream in the absence of oxygen) an important increase of the quantity of carbon present on the surface of the standard mixture (r = 0.5) took place (Table I).

4. Ion Scattering Spectroscopy (ISS). Table II gives the results of ISS measurements.

The sample with r = 0.5 was studied in particular detail. Three types of mixtures were prepared: (I) by simple gentle cogrinding in an agate mortar ("mechanical mixture"); (II) by mixing according to the standard procedure, namely, cosuspension in *n*pentane, followed by evaporation and drying ("standard mixture"); and (III) by impregnation of α -Sb₂O₄ with a solution of ammonium heptamolybdate, followed by calcination at 673 K for 24 h (namely, deliberate contamination).

Samples I and II give the same I_{Mo}/I_{Sb} ratio (0.25). This ratio is half of that observed with contaminated sample III (0.49).

Measurements were repeated after mixture II had worked catalytically for 4 h at 633 K in the presence of oxygen. The I_{Mo}/I_{Sb} ratio remained identical with its value before reaction.

B. Catalytic Activity. Figure 2 presents plots of propionitrile yield vs. sample composition at 623, 633, and 648 K. Standard mixtures of MoO₃ and α -Sb₂O₄ exhibit a strong synergy in N-ethylformamide dehydration. All three curves pass through a maximum at a value of r equal to 0.5. The curves are not symmetrical: higher catalytic activities are observed on the side corresponding to larger MoO₃ contents. The activity of pure α -Sb₂O₄ is very low.

A second series of experiments were carried out in order to follow the deactivation of pure MoO_3 and a two-phase catalyst in the absence of oxygen and their reactivation after reintroduction of oxygen. The results concerning propionitrile yield and selectivity

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Figure 3. Variations of yield and selectivity to propionitrile in deactivation (without O_2) and reactivation (with O_2) tests at 633 K, for the $MoO_3 + \alpha$ -Sb₂O₄ standard mixture (r = 0.5 mass ratio) (curves A, A', a, a') and pure MoO₃ (curves B, B', b, b').

vs. time on stream are given in Figure 3. Propionitrile yields continuously diminished after the oxygen feed was discontinued. A plateau was reached after 2 h (curves A and B). Selectivities to propionitrile also decreased, but some difference in the behavior of the samples was observed (curves a and b): pure MoO_3 exhibited a greater loss in selectivity (curve b) than the two-phase catalyst (curve a); but after 2.5 h, MoO_3 retained a better selectivity for propionitrile. Reactivation of the catalysts by reestablishing the oxygen feed increased both yields and selectivities. The two-phase catalyst regained selectivity more easily than MoO_3 (curves a' and b') and reached a selectivity of 50% after ca. 30 min. This value, lower as for the fresh catalyst, remained constant until the end of the experiment (5 h). The yield for the two-phase catalyst (curve A') increased steadily during reactivation by oxygen in contrast with the case of MoO_3 (curve B').

C. Surface Acidity. Ammonia TPD curves obtained in the first series of measurements mentioned in the Experimental Section are presented in Figure 4a. α -Sb₂O₄ practically does not absorb NH₃ at 298 K. A catalyst which contains a relatively small amount of MoO₃ has a weak surface acidity (curve B). The number of acidic centers increases with the concentration of MoO₃ in the samples. The catalyst containing equal quantities of α -Sb₂O₄ and MoO₃ has more acidic sites (curve C) than pure MoO₃ (curve D). The surface acidity estimated by calibration was 146 and 98 μ mol of NH₃ per gram of sample for curves C and D, respectively.

Figure 4b, obtained with the second procedure described in the Experimental Section on catalyst r = 0.5, indicates that the quantity of acidic sites is changing under the influence of a mild reduction by hydrogen at 423 K (compare curve I and curve C). This reduction decreases surface acidity (initially equivalent to 146 μ mol of NH₃ per gram of sample) by a factor of 3. The catalyst, when reoxidized with oxygen (10% of O₂ in He) at 423 K, reveals a higher acidity (curve I'), which diminishes again after the next reduction (curve II). In the last step, after a new reoxidation, the catalyst regains partly its initial acidity (curve II').

The TPD profiles C and D (Figure 4a) are composed of two overlapping peaks with maxima at 380 and ca. 490 K, respectively. At least two types of sites-relatively weak (380 K) and strong (490 K)—are present. The reduction of samples (Figure 4b) containing MoO₃ always provokes an increase in the number of strong acid sites, in comparison to weak sites.





Figure 4. (a) Ammonia TPD profiles for α -Sb₂O₄ (A), standard mixtures with r = 0.3 (B) and r = 0.5 (C), and MoO₃ (D). (b) Ammonia TPD profiles for the standard mixture, (r = 0.5) after different treatments: reduction with H₂ at 423 K (I); reoxidation with O₂ at 423 K (I'). The next reduction with H₂ (II) and the next reoxidation with O₂ (II').



Figure 5. Mo⁵⁺ ions content per gram of MoO₃ in catalysts, as a function of catalyst composition (curves) and temperature (table). The vertical distance between the experimental points and the dashed straight line corresponding to the same set of results measure the additional Mo⁵⁺ ion content due to the contact of MoO₃ with α -Sb₂O₄. Conditions of pretreatment: (1) 1 h under H₂ at 423 K (\square); (2) treatment 1 + introduction of air at 298 K (\blacksquare); (3) treatment 2 + introduction of air at 423 K for 1 h (O).

D. ESR Studies. Fresh catalysts do not give any ESR signal. The signal appears after contact of the catalyst with hydrogen, e.g., at 423 K. The intensity (eq 2) of the signal (g = 1.93; width ca. 100 G) changes with the temperature of reduction and with composition of the MoO₃ + α -Sb₂O₄ mixtures.

In Figure 5, curves 1, 2, and 3 present variation of the concentration of $(Mo^{5+})_{rel}$ of the Mo^{5+} ion as a function of the treatment cycles described in the Experimental Section. Curve 1 corresponds to samples reduced by hydrogen at 423 K for 1 h. Curves 2 and 3 give the results corresponding to these samples after they have been exposed to air at 298 and 423 K for 1 h, respectively. The dashed straight lines (between ordinate zero for 0% MoO₃ and the experimental points corresponding to 100% MoO₃) indicate the portion of the total Mo⁵⁺ observed which would be due to the corresponding quantity in pure MoO₃. The difference between the experimental points and the corresponding straight lines indicates the presence of the additional Mo⁵⁺ due to the contact of MoO₃ with α -Sb₂O₄ (double arrow in the case of curve 3).

The Mo^{5+} ion concentration $[(Mo^{5+})_{rel}]$ does not change in the range of temperatures 423-523 K (see the table obtained for catalyst r = 0.5, presented in Figure 5).

ESR measurements, similar to those corresponding to curve presented in Figure 5, on a series of catalysts of different composition, reduced by hydrogen at 523 K, indicated the same dependence of Mo⁵⁺ ion concentraton as for reduction at 423 K.

Discussion

In our experiments, only two reactions take place, namely, dehydration to propionitrile and degradation to acetonitrile and CO_2 as shown in scheme 1.

As indicated previously, we focus on the first reaction (to propionitrile), which can be highly selective (ca. 90%). The discussion will concentrate on the active centers and the synergetic mechanism responsible for that first reaction.

The various experiments reported in this work concern (i) catalyst characterization; (ii) the catalytic activity of our catalysts in N-ethylformamide dehydration (Figure 2) and the nature of the acid sites (Figure 4); (iii) the influence of O_2 (Figure 3), which we can presume to modify these catalytic sites; and (iv) the effect of α -Sb₂O₄. The last part comprises general results concerning the reduction and oxidation of our oxides (Figure 5) (which can be due to the surface mobility of oxygen species) and, more generally, the origin of synergy. We shall conduct the discussion by examining in succession those diferent questions.

Characterization. In order to acquire a fundamental understanding of the structure and nature of the catalyst, an analysis with a combination of characterization techniques is necessary.

For a catalyst constituted of two or several phases, several possible modifications of composition or structure during preparation may be contemplated, e.g., formation of a solid solution or a new interface compound, contamination of one phase by another one, or formation of a monolayer of a compound of one phase on the surface of the other. We shall examine all these possibilities in the light of literature and the results of our characterization experiments.

With the MoO₃ + α -Sb₂O₄ system, the formation of ternary Mo-Sb-O compound is very difficult. As stated in the Introduction, Parmentier et al.9 have observed that, for preparing Sb_2MoO_6 or $Sb_2(MoO_4)_3$, it was necessary to heat Sb_2O_3 with MoO₃ in a sealed tube under 600 Torr of argon at 773 K for 24 h. A recalcination of 24 h in the same conditions, after grinding, was necessary to make the reaction between the oxides complete. These new compounds are unstable: when heating in air at 673 K, they decompose into MoO_3 and Sb_2O_4 .⁹ Teller et al.^{11,12} have found a very weak solubility of molybdenum in β -Sb₂O₄ in very severe conditions. MoO₃ and Sb₂O₄ were ground in a mortar and fired in a sealed, evacuated quartz tube at 1123 K for 80 h. At intervals of 24 h, the tube was opened, the mixture was reground and sealed in a fresh tube, and the tube was replaced in the oven. Another important observation found by the authors was that the dissolution of molybdenum always takes place with concurrent transition from α -Sb₂O₄ to β -Sb₂O₄ structure.^{11,12}

The ESR measurements on our fresh catalysts did not detect any signal. The X-ray diffraction spectra of the standard mixtures present only the characteristic lines of the crystalline corresponding to the pure oxides, with no shift. This rules out the presence of solid solutions: only MoO_3 and α -Sb₂O₄ are present in our standard mixtures. No difference in phase composition was observed before and after the catalytic reaction at 623, 633, and 648 K in the presence of oxygen.

XPS (Figure 1 and Table I) detected neither formation of new species which could be attributed to atoms contaminating a surface nor enrichment of an element on the surface of the second phase during the dehydration of N-ethylformamide in the presence of oxygen.

But after 8 h on stream in the absence of oxygen, the intensity of the Mo 3d line decreased, compared to that of Sb $3d_{3/2}$. An important carbon deposition was also detected by XPS. The explanation is that the MoO₃ phase was covered by coke deposits.¹⁷

For investigating surface composition, ISS is more sensitive than XPS. It is hard to imagine that the mixing procedure involving suspension in n-pentane could bring about any contamination, as neither oxide is soluble in *n*-pentane. A gentle mixing by cogrinding could hardly have any substantial effect. The essential identity of the samples is shown by the ISS measurements. The $I_{\rm Mo}/I_{\rm Sb}$ ratio is indeed the same for our standard mixture (r = 0.5) (II) and the sample prepared with cogrinding of the two pure oxides (r = 0.5) (I). The same results had been obtained with BiPO₄-MoO₃ mixtures.⁴ In that case, preparation by suspension in water created a small contamination, due to the slight solubility of MoO₃. In our case too, a deliberate contamination of α -Sb₂O₄ by molybdenum gave, as expected, a much higher I_{Mo}/I_{Sb} ratio. Experiments (XPS) show that this contamination diminishes after the catalytic reaction.¹⁰

For the standard mixture (r = 0.5) (II), this ratio did not change after the catalytic reaction in the presence of oxygen (Table II).

Additional information comes from possible changes of the intensities of the ISS signals during analysis. If surface contamination by element A exists, the A signal should diminish during the measurements, due to erosion of the surface by the 2-keV ions. We do not observe any such effect.¹⁰

All these ISS results show that there is no contamination of α -Sb₂O₄ by molybdenum or of MoO₃ by antimony, neither before nor after the standard mixture has worked catalytically.

Activity and Acid Centers. Pure MoO₃ is active in formamide dehydration, contrary to α -Sb₂O₄. One must conclude that the active sites are situated on MoO_3 . The activity of MoO_3 increases conspicuously in the presence of α -Sb₂O₄.

Comparison of Figure 2 (activity) and Figure 4 (NH₃ TPD) indicates that the most active catalyst (r = 0.5) also exhibits the highest surface acidity; α -Sb₂O₄ possesses no acid sites.

Our results enable a more precise identification of the useful sites. This identification rests on the detection, by NH₃ TPD, of two types of acid sites, designated as "weak" and "strong".

These results should be compared with the findings of Belokopytov et al.¹⁸ and Groff.¹⁹ The authors, in an infrared investigation of the acidity of MoO₃ by NH₃ adsorption, concluded that MoO₃ possesses (i) Lewis acid centers capable of adsorbing ammonia by the formation of a coordination bond and (ii) Brønsted centers, bringing about the formation of NH₄⁺ ion. Surprisingly, the bond between NH_3 and Lewis centers is less strong than that with Brønsted centers.¹⁸ An IR band assigned to NH₃ adsorption on Brønsted sites disappeared only after evacuation at temperatures higher than 473 K. Taking into account those results, one can assign the second TPD peak (490 K) in Figure 4 to NH₃ desorption from Brønsted sites.

The vast majority of mechanisms evoked for explaining dehvdration reactions involves Brønsted acid sites. Previous results in N-formamide dehydration³ led to a similar conclusion, namely, the intervention, in a concerted mechanism, of vicinal Brønsted acid and basic centers:



The present results substantiate our conclusion by showing more directly the presence of Brønsted sites.

Role of O_2 . The originality of the two-phase catalysts containing MoO_3 is that they work efficiently in the dehydration of N-

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^{60.1}

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ethylformamide only in the presence of dioxygen. We must further explain how dioxygen might modify the number of Brønsted acid sites.

As a whole, Figure 4b shows an influence of the reducingoxidizing treatment on both sites (Lewis and Brønsted). But reoxidation of reduced samples gives a conspicuous increase of TPD peaks corresponding to Brøsted sites (please compare curves I and II, corresponding to reduced samples, with curves I' and II', after reoxidation). This increase is more important than that corresponding to Lewis sites.

Generally, Brønsted sites cannot persist on the surface in the absence of water or precursors of hydroxyls. To explain the results in Figure 4b, one takes into account the fact that MoO₃ can retain sufficient hydrogen in its shear structure (or as a MoO₃ "bronze") during the hydrogenation step²⁰ and that this hydrogen could form hydroxyls in the reoxidation step.

The TPD results of Figure 4b thus give proof that oxygen can create or restore the useful Brønsted sites. But this effect may, a priori, be attributed either to new creation of previously destructed acid sites or to cleaning of fouled or clogged, but still existing, sites. XPS indeed indicates coke deposition in severe conditions (without O_2).

The reaction conversion (initial: 28.3% after 8 h on stream without oxygen: 11.2%, for the standard mixture r = 0.5) and the propionitrile selectivity (Figure 3) both changed when O₂ was suppressed from the feed. This implies that part of the centers were fouled (decrease of conversion) and another part altered (decrease of selectivity). In that context, the deactivation observed in the absence of oxygen would be explained by the impossibility of regeneration of Brønsted sites after accidental destruction, when hydroxyls give a water molecule, which escapes. The increase of carbon (XPS) observed together with the decrease in conversion strongly suggests that carbon (coke) is responsible for fouling.

The explanation of the favorable role of oxygen for the selective dehydration of N-ethylformamide to propionitriles should thus take into account both deactivation effects.

With respect to keeping the correct number of acidic sites, the conclusion is that water released by the reaction is not sufficient for maintaining the Brønsted sites. Partial oxidation of hydrogen atoms contained in a small fraction of the reactant (possibly from formamides adsorbed on Lewis sites) might provide the necessary hydroxyls. If we consider the increase of activity observed after reintroducing dioxygen in the feed (Figure 3), we can admit that an additional possibility exists, namely, that H_2O , produced by the catalytic dehydration reaction itself, reacts with reduced Mo ions, giving some hydroxyls. This would probably take place only in the very first stages, upon reintroduction of O_2 .²¹ This effect would be typical of the MoO₃ structure and not linked to the synergetic effects observed with α -Sb₂O₄. If this interpretation is correct, the result of Figure 3, curve B', would correspond to this last mechanism.

On the other hand, we have to consider the possible role of deposited coke. If we admit that, in normal operation (with the corect acidic centers), small amounts of coke are continuously formed on the surface, although at a slower rate than when oxygen is absent, one could imagine that oxygen also continuously cleans the surface from that coke.

It seems to us that oxygen acts in both ways. It certainly acts against the formation of nonselective catalytic sites. There are many reasons to believe that, in addition, it cleans the surface from coke.

Oxygen Spillover and the Role of α -Sb₂O₄. There remains to explain the role of the second oxide, namely, α -Sb₂O₄. All the results presented in this paper strongly support our assumption that α -Sb₂O₄ provides the oxygen species needed by MoO₃ in a more efficient way than MoO3 alone can produce it. Specifically α -Sb₂O₄ would dissociate dioxygen to a mobile oxygen species,

spillover oxygen (O_{SO}) , which would flow to the surface of MoO₃, thus producing or regenerating Brønsted sites.

The existence of a spillover of oxygen is very difficult to prove directly. But some strong indirect proofs exist.

The ESR results show that the movements of oxygen from and to the solid are easier when MoO₃ is in contact with α -Sb₂O₄ (Figure 5). The most straightforward observations concern the removal of oxygen (formation of Mo⁵⁺). They strongly suggest that oxygen needs α -Sb₂O₄ to escape, as O_{SO}, from MoO₃. The flux of diffusion of a surface species can be reversed indeed when the gradient of chemical potential is reversed. The observations correspond to a "reverse spillover", from MoO₃ to α -Sb₂O₄, as was observed in the $MoO_3 + BiPO_4$ system.⁴ The reoxidation effects observed when the MoO₃ + α -Sb₂O₄ mixture is contacted with oxygen (Figure 5, curves 2 and 3) correspond to direct spillover, namely, the process which we postulate for explaining the genesis or regeneration of the Brønsted sites at the surface of MoO_3 .

The variations of selectivity and activity observed upon discontinuation of O_2 supply in the feed and reintroduction (Figure 3) are easily explained if one admits that spillover oxygen (O_{SO}) plays an essential role in creating or regenerating the centers producing propionitrile. Propionitrile selectivity (correlated with the presence of "good" acid centers) varies more when α -Sb₂O₄ is present. Increased drop (curve a) is explained by the escape of O_{SO} through α -Sb₂O₄. More rapid recovery, after reintroduction of O_2 , corresponds to formation of O_{SO} on α -Sb₂O₄, which rapidly "irrigates" MoO₃. The fact that a loss of oxygen takes place in MoO_3 , when the oxygen feed is discontinued, is proven by the XPS results. The binding energy of the Mo 3d band changed after an experiment in the absence of O_2 , indicating a reduction of the Mo^{6+} ion (Figure 1). One can notice, in Figure 3 (curve A'), that the propionitrile yield increases for a longer time when α -Sb₂O₄ is present in the catalyst than with pure MoO_3 . This suggests that some sites that may become inactivated can only be restored by O_{SO} (from α -Sb₂O₄). The diminution of the intensity of the Mo 3d band was interpreted as due to carbon deposition in the tests made without O_2 . The mobile O_{SO} species sent by α -Sb₂O₄ would regenerate the centers inactivated by carbon deposits.

In the previous studies concerning the dehydration of Nethylformamide to nitrile on MoO₃-containing catalysts,^{3,4} we proposed two explanations to the beneficial role of spillover oxygen: either it created or formed again selective sites or it removed carbonaceous deposits from accidentally deactivated sites. The present results indicate that Brønsted sites, which are certainly essential for the reaction, are created or regenerated by the action of oxygen, even in catalysts which had not been contacted with N-ethylformamide. The creation or regeneration of sites (after accidental removal of hydroxyls in dehydration process) thus certainly takes place. But, we cannot exclude that the regeneration of coke deactivated centers also contributes to the overall effect; the effect of α -Sb₂O₄ on recovery of propionitrile yield just mentioned supports this hypothesis.

Our present results confirm that the MoO₃ + α -Sb₂O₄ system works according to the remote control mechanism. Spillover oxygen, O_{SO} , emitted by α -Sb₂O₄, controls the number of selective sites on MoO₃. A very scarce species, O_{SO} , creates, recreates, or regenerates sites which after that can work for many catalytic cycles.

Outlooks

All the oxides we have investigated are components of selective oxidation catalysts. Acidic sites are believed to play a role in selective oxidation. Our results might thus constitute a contribution to the understanding of multicomponent oxidation catalysts.²² Bismuth is indeed believed to play an essential role in the replenishment in oxygen of the bismuth molybdate lattice.^{23,24}

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 α -Sb₂O₄, in our case, also replenishes MoO₃ in oxygen. Our previous results also indicated that Bi as BiPO₄^{2,4} or as Bi₂O₃³ was a gateway to oxygen. The present results show that Sb might play the same role in Mo-containing multicomponent catalysts (Sb-Mo).

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Registry No. EtNHCHO, 627-45-2; EtCN, 107-12-0; MeCN, 75-05-8; NH₃, 7664-41-7; Mo⁵⁺, 22541-84-0; MoO₃, 1313-27-5; α -Sb₂O₄, 1332-81-6; O₂, 7782-44-7.

Evidence of Strong Interaction between Iron Particles and an Activated Carbon Support

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Iron particles of unusual morphology form on the surface of high surface area carbon material. The carbon is pretreated in flowing H₂ at 900 °C prior to metal loading by the incipient wetness technique. Mössbauer spectroscopy indicates that a large fraction of the iron is charge deficient. X-ray, chemisorption, and reaction probes are used to obtain additional information regarding the structure and chemistry of the iron particles. The "point diode" model is used to explain the charge deficiency and the other observations.

Introduction

There is a growing body of evidence that carbon-based supports affect particle morphology and surface chemistry. Only on carbon-based supports have zerovalent metal particles been produced by thermal decomposition of metal carbonyl clusters.^{1–3} On hydroxylated (refractory oxide) supports, metal oxide particles are invariably formed during this process.¹ Particles of unusual morphology (i.e., "rafts") have been produced on carbon supports.^{2,3} It is also well-known that metal particles are more easily reduced on carbon-based supports. The chemistry of carbonsupported particles sometimes differs from that of refractory oxide supported particles.^{4,5} This has sometimes been attributed to enhanced electron transfer between the support and the metal particles.6-8

Mössbauer spectroscopy has frequently been used to examine the structure of small iron particles on carbon-based supports. One feature which has been observed in the Mössbauer spectra of iron particles on a variety of carbon-type supports, and not on any other support material, is a singlet with a large isomer shift.⁵ This feature has previously been attributed to an Fe^{2+} species. In the current work this same singlet is observed for iron particles on yet another carbon-type support; however, unlike the previous cases, in the current work this singlet dominates the Mössbauer spectra. Mössbauer data indicate that there is a small amount of normal metallic iron as well. The X-ray diffraction (XRD), chemisorption, and ammonia reaction probe studies do not reveal any differences between the material formed and normal metallic iron. A new model is advanced to explain all the observations.

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TABLE I: Sample Weight Loadings, Surface Areas, and Significant Impurities^a

	wt % S	wt % O	surface area, m ² /g	
sample			$\overline{P-D^b}$	BET
untreated, unloaded	0.4	8.9	330	280
treated, iron loaded	0.2	11.8	580	480

^aOther elements found in trace amounts (<500 ppm) include Na, Mg, Al, Si, Cl, K, Cu, Ti, Vn, Cr, Mn, Ni, Cu, Zn, Zr, Cd, Pb. ^b Determined by Polyani-Dubinin calculations from CO₂ adsorption. ^c Determined by BET calculations from N_2 adsorption.

It is suggested that the charge deficiency results not from the formation of a chemically unidentified Fe²⁺ species, but rather from change transfer from the iron layer at the iron-carbon interface to the interface itself. It is shown that this model explains all of the data and is completely consistent with the current understanding of metal-semiconductor interfaces. It is clear that this phenomenon can be expected for iron on carbon-type supports, but not for refractory oxide supported iron.

Experimental Section

Catalyst Preparation. Iron particles were produced on a high surface area, wide pore, sulfur-containing carbon extrudate (American Cyanamid lot No. 5507), ground, by impregnation to incipient wetness with an aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O_2$. The substrate was pretreated in flowing H_2 for 10 h at 1173 K. Prior to adsorption, Mössbauer, or kinetic studies, all samples were reduced in situ for 16 h in flowing H₂ at 673 K.

Chemical analysis (Galbraith Laboratories) showed that the dried sample contained 5.2 wt% iron. Substrate impurity levels, Polyani-Dubinin, and BET surface areas⁹ are listed in Table I for both the untreated and treated and metal-loaded material. It should be noted that only sulfur and oxygen are somewhat significant impurities. The pretreatment serves to remove only about

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