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Catalytic synergy via spillover at low temperature: the dehydration and dehydrogenation of *sec*-butanol in the presence of oxygen

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Abstract

This paper reports results concerning the dehydration–dehydrogenation of 2-butanol at low temperatures over mechanical mixtures of oxides: α-$Sb_2O_4 + SnO_2$ and α-$Sb_2O_4 + MoO_3$, where each pure oxide had been prepared separately. The temperatures of reaction were 240°C and 190°C, respectively, for the two mixtures. Both mixtures exhibited better performances than the pure oxides. The α-$Sb_2O_4 + SnO_2$ mixture was not active in 2-butanol dehydration. The yields and the selectivities for butene and/or methyl-ethyl-ketone obtained in the other cases were higher than the theoretical values calculated from the activities of the pure oxides. SBET, XRD and XPS measurements before and after the catalytic reaction did not indicate any change of phase or a contamination during the preparation of the mixtures or during the reaction. The synergetic effects between the phases are therefore explained by the occurrence of a 'remote control mechanism' acting via the migration of spillover oxygen species. These are the first instances of a remote control operating at temperatures of reaction below 250°C. The actions of spillover are the same as at high temperature: creation of new acid sites on MoO_3, regeneration (reoxidation) of the reduced deactivated redox sites on both SnO_2 and MoO_3 and inhibition of the coke formation during the reaction.

Keywords: Dehydration–dehydrogenation of *sec*-butanol; Remote control mechanism; Spillover oxygen; Cooperative effects; Selective oxidation

1. Introduction

Synergetic effects due to interactions between simple oxide phases have often been detected in selective oxidation reactions. A synergy is indicated when the catalytic performances exhibited by intimate mixtures of some (generally two) oxide phases prepared separately, are higher than the properly averaged sum of the activities observed when the pure oxides are tested alone.

Extensive investigations previously carried out in our laboratory allow us to conclude that the most plausible explanation to these cooperative effects is the occurrence of a 'remote con-

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trol mechanism' (RCM). The RCM assumes that some oxides, described as 'spillover oxygen donors', are able to activate molecular oxygen, transforming it to a very active mobile species, namely 'spillover oxygen' (O_{so}). This migrates onto the surface of the other oxides, 'spillover oxygen acceptors', where it creates and/or regenerates the sites active in the selective oxidation reactions. As a result, mixtures of both 'donor' and 'acceptor' phases exhibit much better catalytic performances than those of the individual phases: these are principally enhanced yields and selectivities for the partially oxygenated products, and extended lifetime. We have shown that the RCM correctly explains the cooperative effects observed in selective oxidations and oxidative dehydrogenations, namely butane to maleic anhydride, isobutene to methacrolein, methanol and ethanol to the corresponding aldehydes, ethanol to acetic acid, butene to butadiene, propane to propene, pentane to pentene. Other cases are the dehydro-

Table 1
Summary of the investigations performed in order to evaluate the possibility of mutual contamination between (a) MoO_3 and α-Sb_2O_4 during the oxidation of isobutene to methacrolein and the oxygen-aided dehydration of *N*-ethyl-formamide to propionitrile and (b) SnO_2 and α-Sb_2O_4 during the oxidation of isobutene to methacrolein and the dehydrogenation of butene to butadiene

Catalyst type	Characterization method	Conclusion of the study	Ref.
(a) MoO_3 + α-Sb_2O_4			
Mechanical mixtures of MoO_3 + α-Sb_2O_4	SBET, XRD, XPS, ISS, ESR, SEM, AEM, Zeta potential	No modification of the oxides during the reaction. No new contamination, no solid solution formed	[2], [5], [8], [9], [11], [12], [23], [24]
α-Sb_2O_4 impregnated with Mo ions	SBET, XRD, XPS, ISS, CTEM, AEM	Artificial contamination layer of Mo is destroyed during the reaction: a detachment of the layer and formation of MoO_3 crystallites is observed	[2], [5], [7], [8]
MoO_3 impregnated with Sb ions	SBET, XRD, XPS, ISS, CTEM, AEM	No artificial monolayer of Sb on MoO_3 is formed. Crystallites of α-Sb_2O_4 get larger during the reaction	[2], [5], [7], [8], [11]
Mo-Sb-O mixed phases	XRD, ESR, SEM	Mo-Sb-O mixed phases are unstable in the reaction. Recrystallisation of pure MoO_3 and α-Sb_2O_4 is observed	[2], [5]
(b) SnO_2 + α-Sb_2O_4			
Mechanical mixtures of SnO_2 + α-Sb_2O_4	SBET, XRD, XPS, ESR, SEM, AEM, Zeta potential, Mössbauer	No modification of the oxides during the reaction. No new contamination, no solid solution formed	[2], [4], [7], [11], [24], [25], [26], [27]
α-Sb_2O_4 impregnated with Sn ions	SBET, XRD, XPS, ESR, SEM, AEM, Zeta potential, Mössbauer	The artificially deposited layer of Sn ions detaches. Crystallites of SnO_2 are formed on the surface of α-Sb_2O_4	[28]
SnO_2 impregnated with Sb ions potential, Mössbauer	SBET, XRD, XPS, ESR, SEM, AEM, Zeta	The artificially deposited monolayer of Sb ions detaches. Crystallites of α-Sb_2O_4 are formed on the surface of SnO_2	[7], [28]
Sn-Sb-O mixed phases	SBET, XRD, XPS, ESR, SEM, AEM, Zeta potential, Mössbauer	Mixed phases are formed only at high calcination temperature (600°C). When the concentration of Sb is higher tan 5% (atomic ratio) excess of Sb crystallizes as α-Sb_2O_4 on the surface of SnO_2	[25], [26], [29]

genation of 2-propanol to ketone in the presence of oxygen, and the oxygen-aided dehydration of *N*-ethyl-formamide to propionitrile [1–17].

The most frequent criticism against the RCM originates in the relatively high temperatures (350–450°C) at which cooperative effects have been observed in most of the aforementioned reactions. Under these conditions, it has been argued that some reductions, volatilisations and migrations of the metals of the pure oxides, as well as phase transitions, might be thermodynamically possible and could consequently lead to new catalytic systems, particularly mixed or contaminated oxide phases. According to the authors of these criticisms, such new catalytic systems, even if present in very small amounts on the surfaces of the pure oxides, would exhibit better catalytic performances than the starting oxides. This could thus explain the synergetic effects, thus ruling out the RCM as the most reasonable explanation [2]. This type of approach has been investigated in the case of combination of oxides as bismuth, molybdenum, vanadium and titanium oxides [18–22], but in the case of Sb-Sn-O and Sb-Mo-O systems, these explanations are only speculative and have not yet been supported experimentally. Nevertheless, it seems important to investigate this hypothesis.

The present work shows that synergetic effects between two separately prepared phases, mixed in a very intimate way, occur even at low temperatures (around 200°C compared with 350–450°C in previous works). With these conditions, the possibility to modify the initial catalytic system is thermodynamically precluded or at least highly minimized. It is demonstrated by measurements after the catalytic reaction that no modification of the initial catalysts takes place during the reaction, then the criticism opposed to the RCM therefore turns out to be irrelevant.

This present investigation uses catalysts prepared by mechanical mixtures of oxides synthesized separately, without posterior calcination except a gentle drying at 80°C. Any initial contamination between the mixed phases is totally precluded. Two sets of mixtures, α-$Sb_2O_4 + SnO_2$ and α-$Sb_2O_4 + MoO_3$, were selected. One reason to select these oxides is that they have been previously intensively investigated in selective reactions (oxidation of isobutene to methacrolein, oxygen-aided dehydration of *N*-ethyl-formamide to nitrile, dehydrogenation of butene to butadiene) at relatively high temperatures (350 to 450°C). In all cases, dramatic synergetic effects had been observed. In addition, a very exhaustive investigation using different preparation procedures of the catalysts and several surface-sensitive characterization methods was conducted in order to evaluate the probability to modify the initial catalytic systems during the reaction, particularly with respect to mutual contamination between the phases. Table 1a and Table 1b summarize the conclusions of these studies. For the α-$Sb_2O_4 + MoO_3$ system, it turned out that no mutual contamination took place during the reaction. In complementary experiments, it appeared that artificially contaminated oxides were presenting a trend to decontaminate themselves by recrystallizing in the pure phases during the reaction. Similar results were observed for the α-$Sb_2O_4 + SnO_2$ system, except a weak tendency of the Sb ions to contaminate SnO_2 when the sample was prepared by coprecipitation and calcined at very high temperature (600°C). The conclusion of such researches was that the mutual superficial contamination or mixed phases formation between the oxides was excluded. It was consequently expected that at 'very low temperatures' contaminating phenomena within these mixtures would be completely excluded. Therefore the contaminating phenomena should not explain the observed synergetic effects at low temperature.

In this study, the test reaction was the dehydration–dehydrogenation of 2-butanol to butene and methyl-ethyl-ketone (MEK) in the presence of oxygen. The reaction temperatures were respectively 240°C for the α-$Sb_2O_4 + SnO_2$ system and 190°C for the α-$Sb_2O_4 + MoO_3$ system. The catalysts were characterized before and after the catalytic tests by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) in order to detect possible modifications (e.g. contamination) of the initial catalytic systems respectively in the bulk and on the surface of the samples. Measurement of the specific areas of the samples was also achieved.

2. Experimental

2.1. Catalyst preparation

Pure oxides were prepared separately. α-Sb_2O_4 was obtained by calcination at 500°C during 24 h of a finely ground commercial Sb_2O_3 (Janssen Chimica, 99 + %).

SnO_2 was synthesized by neutralisation (pH = 7) with ammonia (Janssen Chimica, 25 wt% in water) of an aqueous solution (65 g/l) of $SnCl_2$ (Merck, p.a.) previously acidified with some droplets of concentrated HCl (Janssen Chimica). The resulting tin hydroxide was filtered and then carefully washed with distilled water in order to remove chloride anions. The obtained solid was thereafter dried at 110°C during 20 h before being calcined at 600°C during 20 h and at 900°C during 16 h, and ground.

MoO_3 was prepared starting from an aqueous solution (82 g/l) of ammonium heptamolybdate (Merck, extra pure powder) complexed with the same number of equivalents (175 g/l) of oxalic acid (Janssen Chimica, 99 + %). The mixture was stirred at 40°C until obtaining a homogeneous limpid solution. After having removed the solvent under vacuum, the obtained solid was dried overnight at 110°C, decomposed at 300°C during 20 h and calcined at 400°C during 20 h, and ground.

All the phases have been checked by X-ray diffraction to fit, respectively, the patterns of α-Sb_2O_4 cervantite, SnO_2 cassiterite and MoO_3 molybdite phases reported in the ASTM file. Specific surface area of α-Sb_2O_4, SnO_2 and MoO_3 were respectively 0.98 m^2/g, 3.75 m^2/g and 6.30 m^2/g.

Two sets of mechanical mixtures were prepared: α-Sb_2O_4 + SnO_2 and α-Sb_2O_4 + MoO_3. They were prepared by vigorously mixing (1° ultraturax: 10 min–6000 rpm, 2° ultrasonication: 10 min) a well dispersed suspension (10 g of oxide/l) of adequate quantities of both pure oxides in *n*-pentane. After removing the solvent under vacuum at room temperature, the catalysts were gently dried overnight at 80°C. The mixtures were not submitted to further thermal treatments. Different compositions of mixtures were prepared based on the mass ratio (R_m = 0.25, 0.5, 0.75) as defined in Eq. (1).

$$R_m = \frac{\text{mass oxide A}}{\text{mass oxide A} + \text{mass oxide B}} \qquad (1)$$

with A: MoO_3 or SnO_2 and B: α-Sb_2O_4.

The pure oxide phases, SnO_2 ($R_m = 0$), MoO_3 ($R_m = 0$) and α-Sb_2O_4 ($R_m = 1$), were treated following exactly the same procedure as the mechanical mixtures.

2.2. Catalytic activity measurement

Catalytic tests were performed in a fixed bed reactor working at atmospheric pressure. The partial pressure of 2-butanol was 176 mmHg balanced with air. The total flow was 90 ml/min. For each test, 500 mg of catalyst were used with a granulometry between 500 and 800 μm. The temperature of reaction was fixed at 190°C for α-Sb_2O_4 + MoO_3 catalysts (as in other publications dealing with the same reaction [30]), and at 240°C for α-Sb_2O_4 + SnO_2 catalysts (in order to have an activity high enough for allowing a proper discussion of the catalytic results). After having reached the steady state, the activity of the catalysts was measured during 3 h. The reactor was then cooled down to room temperature in the same stream as during the reaction.

The proportions of non converted 2-butanol, and the products of the reaction, butene (But) and methyl-ethyl-ketone (MEK) at the reactoroutlet were determined by gas chromatography. Catalytic activity is reported in terms of conversion of 2-butanol (%C, number of moles of 2-butanol converted per 100 moles of 2-butanol introduced), yields ($\%Y_{\mathrm{MEK}}$ and $\%Y_{\mathrm{But}}$, number of moles of MEK or But produced per 100 moles of 2-butanol introduced) and selectivities ($\%S_{\mathrm{MEK}}$ and $\%S_{\mathrm{But}}$, number of moles of MEK or But produced per 100 moles of 2-butanol converted).

For each mechanical mixture with a mass ratio R_m, theoretical values for these expressions have been calculated based on the properly averaged sum of the activities measured for the pure oxides, as described in Eqs. (2). These theoretical values are representative of the activity of a biphasic catalysts where the constituting phases perform the catalytic reaction without mutual interaction (namely, as if they were alone in the reactor) supposing, as a first approximation, zero-order reactions.

(a) Theoretical conversion:

$$\%C_{\mathrm{th}}^{R_m} = R_m \times \text{Conversion of pure A} + (1 - R_m) \times \text{Conversion of the pure } \alpha\text{-}Sb_2O_4$$

(b) Theoretical yield (But or MEK):

$$\%Y_{\mathrm{th}}^{R_m} = R_m \times \text{Yield of pure A} + (1 - R_m) \times \text{Yield of the pure } \alpha\text{-}Sb_2O_4$$

with A: MoO_3 or SnO_2.

(c) Theoretical selectivity (But or MEK):

$$\%S_{\mathrm{th}}^{R_m} = \%Y_{\mathrm{th}}^{R_m} / \%C_{\mathrm{th}}^{R_m} \quad (2)$$

2.3. Characterization

Each catalyst was characterized before and after the catalytic test by specific surface area measurement (SBET), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

SBET of the samples was measured assuming the single point approximation of the BET equation for the adsorption of nitrogen at 77 K on a Micromeritics Flowsorb II.

XRD was performed on a Siemens D5000 Kristalloflex diffractometer. Spectra were recorded using the Cu $K_{\alpha 1,2}$ radiation ($\lambda = 1.5418$ Å) in the symmetric 2θ mode between 2 and 90°.

XPS analysis were achieved on a VG MKII spectrometer using a Mg anode ($K_\alpha = 1253.6$ eV). The C_{1s}, $Sb_{3d5/2}$, $Sn_{3d5/2}$ and $Mo_{3d5/2}$ bands were recorded. The contamination C_{1s} line was selected as the kinetic energies reference, at a value of 284.8 eV. Wagner sensibility factors were used in order to quantify the different elements on the surface [31]. The Si_{2p} peak of a dry commercial Crossfields Chemicals silica was used as external reference for calculating the relative surface 'concentration' $I_{\mathrm{rel}}(M)$ [Eq. (3)]. This quantity was used in order to compare the composition (metals and deposited coke) of the XPS-analyzed portion (a near surface layer of some nanometers in thickness) of the different samples.

$$I_{\mathrm{rel}}(M) = I_M / I_{\mathrm{Si2p}} \quad (3)$$

where M is C_{1s} or $Sb_{3d5/2}$ or $Sn_{3d5/2}$ or $Mo_{3d5/2}$ peaks, and I the integral of the corresponding peak normalized with the number of scans recorder, the energy window analyzed, the number of channels recorded on the energy window, and the Wagner sensibility factor [31] of the considered element.

3. Results

3.1. Catalytic results

Tables 2 and 3 present the catalytic activities measured, respectively, for the α-Sb_2O_4-SnO_2 and for the α-Sb_2O_4-MoO_3 mixtures. In both systems, important synergetic effects between the two phases were observed.

3.1.1. System α-Sb_2O_4-SnO_2 (Table 2)

α-Sb_2O_4 was completely inactive both for the dehydration and dehydrogenation of 2-butanol. No butene was produced in the catalysts con-

Table 2
Measured and theoretical values calculated according Eq. (2), supposing no synergetic effects (in parenthesis): conversion of 2-butanol (%C), yields (%Y_{MEK} and %Y_{But}) for MEK and butene and selectivity (%S_{MEK}) for MEK at 240°C for the α-Sb_2O_4-SnO_2 system

R_m	%C	%Y_{But}	%Y_{MEK}	%S_{MEK}
0 (α-Sb_2O_4)	0	0	0	
0.25	1.8 (2.9)	0	1.8 (2.4)	100 (82)
0.5	8.3 (5.9)	0	7.6 (4.9)	91.5 (82)
0.75	9.7 (8.9)	0	9.7 (7.3)	100 (82)
1 (SnO_2)	11.9	0	9.8	82

taining SnO_2. This indicated that neither α-Sb_2O_4 nor SnO_2, tested alone or in mixtures, possessed acid sites active for 2-butanol dehydration. But the mixtures of α-Sb_2O_4 and SnO_2 exhibited cooperative effects when considering both the conversion of 2-butanol, the yield and the selectivity for MEK. Only the mixture containing 25% of SnO_2 did not present an enhancement in the conversion and the yield for MEK. In this case, only an increase in the selectivity was observed. However, for this mixture the result was not totally significant as the conversion was very low near the range of the limit of detection of the analysis method used.

3.1.2. System α-Sb_2O_4-MoO_3 (Table 3)

Pure MoO_3 was highly active, producing mainly butene and also a small amount of MEK. For the mixtures containing α-Sb_2O_4 and MoO_3, cooperative effects between the two phases were observed. All the mechanical mixtures presented higher conversion of 2-butanol, and yields (with maintained selectivities) both for butene and MEK than the values calculated theoretically as if no synergy existed.

3.2. Characterization results

3.2.1. Specific area measurement

Table 4a and Table 4b present the SBET values obtained before and after the tests for the systems α-Sb_2O_4-SnO_2 and α-Sb_2O_4-MoO_3, respectively.

For pure oxides and their mechanical mixtures, there was a slight increase of the SBET values after the reaction. A modification of the SBET of a catalyst during the reaction has already been reported to be possibly due to the coke deposition on its surface [2,5,25, 26,28,29,32]. However, in the present case, the variations of SBET were relatively weak for allowing an unquestionable correlation with the coke formation.

On the other hand, as the SBET have only slightly increased, it turned out that no important abrasion phenomenon of the particles of catalysts occurred during the reaction. Moreover, as the relative increases were constant for all the samples (about 10%), another indication is that the particles in the mechanical mixtures have not been subjected to a more important abrasion than the particles of pure oxides. Consequently, this meant that the synergetic effects reported in the previous section could not be explained by higher active surfaces developed by the particles in the mechanical mixtures than in the pure oxides.

Table 3
Measured and theoretical values calculated supposing no synergetic effects (in parenthesis): conversion of 2-butanol (%C), yields (%Y_{MEK} and %Y_{But}) and selectivities (%S_{MEK} and %S_{But}) for MEK and But at 190°C for the α-Sb_2O_4-MoO_3 system

R_m	%C	%Y_{But}	%Y_{MEK}	%S_{But}	%S_{MEK}
0 (α-Sb_2O_4)	0	0	0	–	–
0.25	18.4 (13)	4.9 (4.7)	1.75 (0.5)	26.6 (36)	9.4 (3.6)
0.5	36.8 (26)	13.2 (9.4)	1.9 (0.9)	36 (36)	5.1 (3.6)
0.75	58.7 (39)	20.5 (14.1)	2.6 (1.4)	35 (36)	4.4 (3.6)
1 (MoO_3)	52	18.8	1.9	36	3.6

Table 4

R_m	SBET before test (m^2/g)	SBET after test (m^2/g)
(a) Specific surface area values (SBET) of the catalysts from the α-Sb_2O_4-SnO_2 system before and after the catalytic tests		
0 (α-Sb_2O_4)	0.98	1.11
0.25	1.825	2.03
0.5	2.84	3.03
0.75	3.82	4.23
1 (SnO_2)	3.75	4.26
(b) Specific surface area values (SBET) of the catalysts from the α-Sb_2O_4-MoO_3 system before and after the catalytic tests		
0 (Sb_2O_4)	0.98	1.11
0.25	2.40	2.40
0.5	3.73	4.24
0.75	5.09	5.34
1 (MoO_3)	6.30	6.94

3.2.2. *X-ray diffraction*

Pure oxides subjected to a preparation procedure identical to that applied to the mechanical mixtures exhibited X-ray diffraction patterns completely identical to the ones obtained before this treatment. Before catalytic tests, the mechanical mixtures showed all the lines of their composing pure oxides with intensities proportional to the amount of these oxides in the mixture. No other features were observed.

When characterized after the catalytic tests, both pure oxides and mechanical mixtures presented patterns totally identical with the ones obtained before. No shift in peak diffraction angles, disappearance of peak, nor appearance of new peaks were detected.

3.2.3. *X-ray photoelectron spectroscopy*

For both pure oxides and mechanical mixtures, the binding energies for the $Sn_{3d5/2}$ and for the $Mo_{3d5/2}$ bands were unchanged after the catalytic tests. The binding energies were characteristic of Sn^{4+} and Mo^{6+} species respectively. Small amounts of Mo^{5+} were detected, before tests, in the samples containing MoO_3, but disappeared after the reaction. Owing to the composition of the cervantite phase, the $Sb_{3d5/2}$ line should theoretically exhibit a doublet corresponding to the Sb^{3+} and Sb^{5+} species present in even quantities [4,5]. Nevertheless, an unquestionable distinction between these two features is impossible because the difference in the corresponding binding energies is about 0.5 eV, which is close of the resolution of our spectrometer. No change of the shape of the outside envelope of the doublet was observed, indicating a constant Sb^{3+}/Sb^{5+} ratio. Thereafter, the $Sb_{3d5/2}$ band was consequently considered as a single band. The binding energy corresponding to this band remained unchanged after tests,

Table 5

R_m	$I_{rel}(C)$	$I_{rel}(Sb)$	$I_{rel}(Sn)$
(a) Relative concentrations $I_{rel}(M)$ calculated from the XPS data for the α-Sb_2O_4-SnO_2 catalysts. Values in parentheses were obtained after the catalytic tests			
0 (Sb_2O_4)	0.81 (0.71)	0.84 (0.77)	
0.25	0.88 (0.73)	0.34 (0.40)	0.37 (0.32)
0.5	0.91 (0.70)	0.20 (0.27)	0.58 (0.60)
0.75	0.74 (0.71)	0.11 (0.10)	0.72 (0.72)
1 (SnO_2)	0.72 (0.76)		0.82 (0.79)
(b) Relative concentrations $I_{rel}(M)$ calculated from the XPS data for the α-Sb_2O_4-MoO_3 catalysts. Values in parentheses were obtained after the catalytic tests			
R_m	$I_{rel}(C)$	$I_{rel}(Sb)$	$I_{rel}(Mo)$
0 (Sb_2O_4)	0.81 (0.71)	0.84 (0.77)	
0.25	1.34 (0.86)	0.28 (0.20)	0.43 (0.41)
0.5	0.74 (1.00)	0.20 (0.10)	0.48 (0.51)
0.75	0.81 (0.93)	0.05 (0.04)	0.65 (0.58)
1 (MoO_3)	0.75 (0.98)		0.71 (0.60)

namely perfectly fitting the fresh pure α-Sb_2O_4 spectrum.

Table 5a and Table 5b report the relative concentrations calculated from the XPS data according to Eq. (3).

The I_{rel}(Mo) and I_{rel}(Sn) relative values logically increased when the concentration of MoO_3 or SnO_2 in the mixtures increased. Simultaneously, the I_{rel}(Sb) values decreased. In both catalytic systems investigated, I_{rel}(Sb), I_{rel}(Mo) and I_{rel}(Sn) relative concentrations remained constant when comparing the values before and after the catalytic tests. No measurable enrichment of the surface of the catalyst, in any of the metals involved, occurred during the reaction.

As concerns the pure oxides, α-Sb_2O_4 exhibited a slightly lower coke level ($I_{rel}(C)$ relative concentrations) after the test than before. On the contrary, MoO_3 presented a higher $I_{rel}(C)$ relative concentration after the test, while SnO_2 kept it relatively constant during the reaction.

For all the mechanical mixtures of α-Sb_2O_4 and SnO_2, a decrease of the coke level was observed on the catalysts after the reaction. The importance of this effect presented the trend to get higher with higher concentrations of α-Sb_2O_4 in the mixtures. A similar behaviour was observed for the mixtures of α-Sb_2O_4 with MoO_3. The mixture containing 75% of α-Sb_2O_4 ($R_m = 0.25$) presented a significant reduction of the $I_{rel}(C)$ relative concentration after the test. For the other mixtures, a slight increase of the amounts of coke on the surface of the catalysts was observed, but that increase was smaller for the mechanical mixtures than when MoO_3 was reacted alone.

4. Discussion

4.1. Absence of contamination between the phases, mixed phase or solid solution

Summarizing, there is no indication of any change in the phases present in the catalysts after the pure oxides are mixed or after the catalytic test.

On the other hand, there is absolutely no indication that special structures form on the surface. Within the sensitivity limits of the techniques used, no special oxidation states or changes of surface composition are detected. In particular, there is no indication that metals from one oxide would spread on the other, although we have used a very sensitive approach for detecting such effects: measurement of the ratio of the signal intensities with respect with an external standard (silica).

In line with the results obtained previously with these same catalytic systems, as recalled in the beginning of this article, we must take into account the presence of unmodified and uncontaminated phases for interpreting the results. This will be done in the next section.

4.2. Discussion of the catalytic results

The results can be easily explained coherently by the existence of a ‘remote control mechanism’ (RCM) via the migration of ‘spillover oxygen (O_{so})’ species.

Previous publications demonstrated that α-Sb_2O_4 is playing the role of the ‘O_{so} donor’ phase, with SnO_2 and MoO_3 acting as the ‘O_{so} acceptors’. This conclusion was reached on the basis of experiments carried out at high temperatures [4,5]. The cooperative effects detected in the present work show that they play the same roles at low temperatures.

The synergetic effects observed here are somehow weaker than the ones previously obtained at about 400°C over the same type of catalysts. The explanation is the fact that α-Sb_2O_4 activates a smaller amount of molecular oxygen to spillover species at low than at high temperatures. The cooperative effects, due to the action of O_{so} on the active phases, are thus logically less pronounced: (i) lower synergetic effects when considering the conversion, the yields and the selectivities, (ii) coke formation (when it occurs) only slowed down in place of a significant or complete removal at high temperatures. Nonetheless, the consequences of the

RCM at low temperature of reaction remains qualitatively the same as at high temperatures.

4.2.1. *Creation of new active acid sites*

The characterization of mechanical mixtures MoO_3-α-Sb_2O_4 have previously shown that an effect of O_{so} produced by α-Sb_2O_4, where it reacts with MoO_3, was an increase of the Brönsted acidity of its surface. A direct correlation between the amount of Brönsted sites and their activity in the oxygen-aided dehydration of *N*-ethyl-formamide, which is achieved on acid sites, had been observed [32]. The dehydration of 2-butanol is also catalysed by Brönsted acid sites. The improvement of the activity obtained when MoO_3 is mixed with α-Sb_2O_4 is therefore attributed to the increase of its acidity under the action of O_{so}. This explains the higher yields with maintained selectivities to butene observed when MoO_3 is mixed with α-Sb_2O_4.

4.2.2. *Inhibition of the deactivation of redox sites*

Experiments have previously shown that an effect of O_{so} was to help the reoxidation of slightly reduced MoO_3 [32]. The dehydrogenation of 2-butanol occurs on redox sites of the catalysts. The deactivation of these sites mainly consists in their slight reduction. In both α-Sb_2O_4-MoO_3 and α-Sb_2O_4-SnO_2 systems, an increase of the yields to MEK was observed when α-Sb_2O_4 was added. This improvement can thus be explained by the action of O_{so} which inhibits the reduction of the metals of the redox sites in the conditions of reaction and maintains them in the oxidized coordinations which are active for the selective oxidation reactions. This effect is similar to the ones observed in the oxidative dehydrogenation of other alcohols [10].

4.2.3. *Inhibition of coke deposition*

IR and XPS studies have previously shown that O_{so} is able to inhibit the formation of the coke precursors on the surface of the catalysts. It has also been shown that O_{so} triggers the elimination of the coke from the surface of an artificially coked MoO_3 [32]. In the presence of α-Sb_2O_4, MoO_3 exhibits a lower coke deposition on its surface. In mechanical mixtures, coke was removed from the surface of SnO_2, α-Sb_2O_4 inhibits the formation of coke precursors during the reaction on the surface of SnO_2. The effect observed here is in direct line with previous results [33].

The general consequence of these 3 effects of O_{so} is that the number of active sites both for the dehydration and the dehydrogenation of 2-butanol is higher when either MoO_3 or SnO_2 are tested in the presence of α-Sb_2O_4. Consequently this explains the higher conversion of 2-butanol measured for all the mechanical mixtures than for the pure MoO_3 and SnO_2.

The importance of these new results is that we show that the effects take place at much lower temperature than in previously studied systems, namely 190–240°C instead of 380–450°C.

5. Conclusion

Synergetic effects have been observed at low temperatures in the dehydration-dehydrogenation of 2-butanol in the presence of oxygen between α-Sb_2O_4 and SnO_2, and between α-Sb_2O_4 and MoO_3. The characterization of the catalysts has undoubtedly discarded the possibility of a modification of the starting oxides by mutual contamination or another mechanism. Consequently, the synergetic effects can be explained most correctly by a remote control mechanism between separate phases in intimate contact. In agreement with previous investigations, α-Sb_2O_4 plays the role of the spillover oxygen donor, while MoO_3 and SnO_2 are the spillover oxygen acceptor phases. At low temperatures, probably only small quantities of O_{so} are activated, thus triggering slight cooperative effects between the phases. Nevertheless, the effects of O_{so} remain identical to the ones at high temperatures: (i) creating new Brönsted acid sites on MoO_3, (ii) maintaining the redox sites on MoO_3 and SnO_2 in their selective oxidation states, (iii) inhibiting coke formation.

This constitutes the very first instances of remote control processes occurring at temperatures around 200°C. By making very highly improbable the main criticism opposed to the RCM, namely mutual contamination and modification of the initial catalytic system, the present investigation confirms the validity of the mechanism proposed for the cooperative effects at high temperatures.

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