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Synergetic effects in multiphase catalysts: the role of $FeSbO_4$ as donor–acceptor of spillover oxygen

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Abstract

The present work reports experimental data to further investigate the role of $FeSbO_4$ in multiphase catalysts used in the selective oxidation of isobutene to methacrolein. Its oxygen acceptor and donor properties have been evaluated by showing the effect of admixed α-Sb_2O_4, which is a good oxygen donor able to increase the selectivity of an acceptor phase, and of MoO_3 which generally acts as a good oxygen acceptor, namely carries all the functions necessary for oxidation, but has only a weak ability to dissociate oxygen. Catalysts containing $FeSbO_4$ and α-Sb_2O_4 or MoO_3 were prepared: (1) by mechanical mixture; and (2) by artificial deposition of Sb and Mo ions on $FeSbO_4$. The catalysts were characterized, before and after the test, by S_{BET}, XRD and XPS. The mechanical mixtures and impregnated catalysts gave a synergy in the yield and in the selectivity to methacrolein. Characterization shows that the catalysts are formed by two separate non-contaminated phases in contact. Synergy is explained by the remote control mechanism. It is proposed that $FeSbO_4$ act as a donor of oxygen spillover when it is mixed with MoO_3, and as an acceptor in presence of α-Sb_2O_4.

Keywords: Multiphase catalysts; $FeSbO_4$; Spillover oxygen

1. Introduction

It is now well established that oxide catalysts which present the best catalytic selectivities in the selective oxidation of hydrocarbons contain several phases. The $FeSbO_4$ phase is frequently present in such catalysts. It is also known that the best selectivities are obtained when the surface of $FeSbO_4$ is enriched in Sb [1]. It has been proposed in the literature that Sb in excess covers the $FeSbO_4$ surface as Sb_2O_4, either as crystallites [2] or as an Sb layer [1]. However, many discrepancies exist in these investigations as to the reasons why selectivities are higher when $FeSbO_4$ is enriched by Sb.

The role of Sb might be: (a) to inhibit the formation of free Fe_2O_3 and to suppress total oxidation [3]; (b) to react with $FeSbO_4$ to form a surface phase, $FeSb_2O_6$ [1]; (c) to increase the surface density of O=Sb=O double bonds [4]; or (d) to create an epitaxial structure on $FeSbO_4$. In this case, it was considered that α-Sb_2O_4 crystallites were oriented on the surface of $FeSbO_4$ and thereby could create catalytically active sites not found in either of the isolated phases [2].

Several investigations have been conducted

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in our laboratory [5–10] in order to study synergetic effects in biphasic catalysts in the oxidation of hydrocarbons. These studies showed that there is often a cooperation involving non-contaminated phases. This corresponds to an increase in the selectivity and is explained by a remote control mechanism, RMC. According to this mechanism, spillover oxygen, O_{so}, produced by a donor phase can react with the surface of an acceptor of O_{so}, modifying the properties of the catalytic sites on the acceptor phase.

In these studies, we carefully took into account alternative explanations of the cooperation observed, in particular, a possible mutual contamination or formation of new compounds. Our results led to a classification of the oxides used in multicomponent catalysts as donor–acceptor or intermediary behaviour [5,6], α-Sb_2O_4 being a pure donor and MoO_3 a pure acceptor of O_{so}. It is possible to locate most oxides used in selective oxidation on a donor–acceptor scale. Many oxides have a dual behaviour, as evidenced by Bi_2MoO_6 [5,10] in the oxidation of isobutene to methacrolein. This oxide is moderately active and selective in this reaction, but its catalytic properties could be improved by adding phases such as SnO_2 (acceptor) or α-Sb_2O_4 (donor). The present work will show that $FeSbO_4$ can also play a dual role (donor–acceptor of O_{so}) during the selective oxidation of isobutene to methacrolein.

We applied a strategy similar to the one followed to study synergetic effects in α-Sb_2O_4 + MoO_3 [11,12] and α-Sb_2O_4 + SnO_2 [13,14]. Biphasic catalysts were prepared by mechanically mixing $FeSbO_4$ with either a donor or an acceptor. α-Sb_2O_4 was selected as donor and MoO_3 as acceptor. In order to minimize the contamination between the oxides, the mechanical mixtures were obtained by dispersing the separately prepared oxides ($FeSbO_4$ + MoO_3 and $FeSbO_4$ + α-Sb_2O_4) in *n*-pentane, evaporating the solvent and drying without further calcination. The role played by the contamination was evaluated by studying the stability of minute artificial deposits of Sb and Mo ions on $FeSbO_4$. In order to study the solid state modifications of the catalysts during the catalytic reaction, catalysts were characterized before and after the test by S_{BET}, XRD and XPS.

2. Experimental

2.1. Catalyst preparation

2.1.1. Single phase catalysts

$FeSbO_4$ was prepared by the citrate method (sample denoted $FeSbO_4$ CT) [15] and by coprecipitation (sample denoted $FeSbO_4$ CP).

2.1.2. Citrate method

An amount of 150 ml of a transparent aqueous solution containing 34.7 g of $Fe(NO_3)_3 \cdot 9H_2O$ (Merk, p.a. grade) was mixed with 100 ml of a solution containing 25.6 g of $SbCl_5$ (Aldrich, p.a. grade) and HCl. Then a quantity of citric acid corresponding, in equivalent grams, to 1.1 times the quantity of metal was added. The orange solution was evaporated in a Rotavapor at 308 K until a viscous solution was obtained. This solution was dried under vacuum at 373 K for 16 h, giving an amorphous solid organic compound. Finally, a certain amount of this solid was decomposed at 473 K for 2 h and then calcined at 673 K for 2 h and 973 K for 4 h, and the sample was denoted $FeSbO_4$ CT1. Another portion was decomposed at 573 K for 6 h and then calcined at 773 K for 24 h ($FeSbO_4$ CT2).

2.1.3. Coprecipitation method

A similar procedure was used, except that citric acid was not added. The viscous orange solution obtained after evaporation during 1 day in a Rotavapor at 308 K was dried at 373 K for 16 h. The solids were then calcined at 773 K for 17 h and 1073 K for 5 h, respectively (denoted as $FeSbO_4$ CP1).

α-Sb_2O_4 was prepared by calcination of

Sb_2O_3 in air at 773 K for 20 h. MoO_3 was obtained by calcination of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (AHM) in air at 773 K for 20 h.

2.1.4. Two-phase catalysts

(a) Mechanical mixtures. The following mixtures were prepared: (1) $FeSbO_4$ CP1 with MoO_3; and (2) $FeSbO_4$ CT1 with α-Sb_2O_4. The mixtures were prepared by vigorously mixing the suspension of the powders in 200 ml of *n*-pentane for 3 min by means of a mixer (Ultra-Turrax from Janke and Kunkel) at room temperature. After evaporation of the *n*-pentane under reduced pressure, the mixtures so obtained were dried in air at 323 K overnight. Mechanical mixtures were not calcined after preparation. The composition of the mechanical mixtures is expressed as the mass ratio, R_m = weight A/(weight A + weight B), where A is $FeSbO_4$ and B is α-Sb_2O_4 or MoO_3. The R_m values are 1.0 (pure $FeSbO_4$), 0.5 and 0.0 (pure α-Sb_2O_4 or MoO_3).

(b) Impregnated catalysts. $FeSbO_4$ (CT or CP) was impregnated with quantities corresponding to those necessary to form 0.25 and 1.5 monolayers ('nominal loading') of Sb or Mo ions (denoted as $FeSbO_4/L$, L = number of monolayers). The quantity of antimony necessary to form 0.25 and 1.5 monolayers of α-Sb_2O_4 on the surface of $FeSbO_4$ CT2 was calculated on the basis of the BET surface area of $FeSbO_4$ CT2 (7.3 m^2/g) and the area covered by one molecule of α-Sb_2O_4. We took as a basis the larger exhibiting (100) face of α-Sb_2O_4. The area covered by a unit cell of α-Sb_2O_4 is estimated at 0.16 nm^2 [13]. Values of 0.57 and 3.33% were calculated for the percentage in weight of α-Sb_2O_4 to introduce. The percentage in weight of MoO_3 necessary to form 0.25 and 1.5 monolayers of MoO_3 on the surface of $FeSbO_4$ CP1 (S_{BET} = 2.5 m^2/g) were calculated similarly. The surface covered by one molecule of MoO_3 is 0.17 nm^2 [11]. The values correspond to 8.0 and 36.0% in weight.

The impregnation of $FeSbO_4$ CT2 with Sb ions was realized with a $CHCl_3$ solution containing $SbCl_5$ and $SbCl_3$ ($Sb^{3+}/Sb^{5+} = 1$). Slow evaporation of the solvent was performed in the Rotavapor at 308 K under reduced pressure. The powder thus obtained was washed with a very dilute NH_3 solution in order to eliminate Cl^-. The samples were then dried at 383 K overnight.

The impregnation of $FeSbO_4$ CP1 with Mo ions was made with an aqueous solution of AHM. The same procedure to that indicated above was used for drying and calcining these catalysts. Part of these Mo-impregnated samples were calcined at 713 K for 5 h.

2.2. Catalyst characterization

All catalysts were characterized before and after the catalytic test using:

1. *BET*. The catalyst surface areas, S_{BET}, were measured by adsorption of krypton at 77 K by the BET method using a Micromeritics Asap 2000 instrument.
2. *XRD*. XRD patterns were obtained with a high resolution X-ray diffractometer Siemens D5000 using Ni-filtered Cu-Kα1 radiation (λ = 1.541 Å).
3. *XPS*. XPS analyses were performed with an SSX-100 model 206 X-ray photoelectron spectrometer from FISONS. The analysis chamber was operated at a pressure close to 5×10^{-9} torr. The C1s, Mo3d, O1s, Sb3d, Fe2p, and C1s bands were swept successively. The binding energy (BE) values were calculated using C1s as a reference (BE of $\underline{C}$–C,H fixed at 284.8 eV). SiO_2 was additionally used as an external standard.

2.3. Catalytic tests

The catalytic tests were carried out in a continuous gas-flow fixed bed reactor with a pyrex U-tube reactor of 8 mm i.d. operating under atmospheric pressure. The catalyst (particle size between 500 and 800 μm) was packed in the central section of the reactor between glass pills of 1 mm in diameter. The feed consisted of a mixture of isobutene, oxygen and helium with partial pressures of 76, 152 and 532 torr, respectively; total feed was 36 ml/min and reaction temperature 693 K. The total amount of catalyst used was 200 mg in the case of the mechanical mixtures containing $FeSbO_4$ CP1 and MoO_3 as well as $FeSbO_4$ CP1 impregnated with Mo ions; 600 mg were used for the $FeSbO_4$ CT1 + α-Sb_2O_4 mechanical mixture, and 225 mg for the impregnated $FeSbO_4$ CT2 with Sb ions. The volume of the catalyst bed was 0.9 or 3.4 cm^3. The corresponding contact time was 1.63 and 6.18 s, respectively. Analysis of reactants and products was realized by gas-phase chromatography (Intersmat IGC 120 ml), using a catharometer. Two columns were used, a Tenax for analyzing methacrolein and other oxygen-containing products (acrolein, alcohols) and a Porapak Q to separate isobutene, CO_2, N_2 and water. The main reaction products were methacrolein, CO_2 and water. Results presented correspond to the catalytic performances after 3 h of reaction.

2.4. Expression of the synergetic effects

The synergetic effects on the conversion are calculated on the assumption of a zero order reaction. Taken as a first approximation they are expressed by the following formula: $\mathrm{Syn}^C = C_{AB} - C_{(A+B)}/C_{(A+B)} \times 100$, where C_{AB} is the conversion of the mixture and $C_{(A+B)}$ is the theoretical conversion in the absence of synergetic effect, namely $C_{(A+B)} = R_m \cdot C_A + (1 - Rm) \cdot C_B$, in which C_A and C_B are isobutene conversion of single phase catalysts A and B, respectively. A similar equation can be obtained for the yield in methacrolein, Syn^Y. For the selectivity, the synergetic effect is defined as $\mathrm{Syn}^S = \Delta S/S_{(A+B)} \times 100$ in which $\Delta S = S_{AB} - S_{(A+B)}$, where S_{AB} is the selectivity of the mixture and $S_{(A+B)}$, the selectivity which would be observed in the absence of any synergetic effect, defined for a mixture with R_m, as $(Y_{(A+B)})/(C_{(A+B)})$. For the synergetic effect on the yield in CO_2, a similar equation as for the yield in methacrolein was used.

3. Results

3.1. Characterization

3.1.1. BET surface area

The surface area of MoO_3 is 5.1 m^2/g, of α-Sb_2O_4 is 2.0 m^2/g, of $FeSbO_4$ CP1 is 2.5 m^2/g, of $FeSbO_4$ CT1 is 3.9 m^2/g and of $FeSbO_4$ CT2 is 7.3 m^2/g.

3.1.2. The mechanical mixtures

$FeSbO_4$ CP1 + MoO_3 and $FeSbO_4$ CT1 + α-Sb_2O_4 show surface areas corresponding to the properly averaged sum of those measured for the single oxides. No difference between fresh and used samples was detected.

For the $FeSbO_4$ CP1 impregnated with Mo ions, the BET surface areas decrease (by about 25%) after Mo loading and increase either after calcination (by about 50%) or after the test (by about 100%). In the case of $FeSbO_4$ CT2 impregnated with Sb ions, a decrease (by about 20%) of the BET surface areas is observed after Sb loading. No change is observed after the test.

3.1.3. XRD

The XRD pattern of the antimony oxide corresponds to α-Sb_2O_4 (cervantite). Patterns of $FeSbO_4$ CT2 correspond to that of iron antimony oxide. X-ray pattern excludes the presence of $FeSb_2O_6$ (trypuhyite) in the samples. In $FeSbO_4$ CT1 and CT2, the presence of Fe_2O_3 hematite was observed. The most intense peaks of $FeSbO_4$ and Fe_2O_3 ($2\theta = 27.23$ and $2\theta = 33.2$, respectively) were used to calculate the $FeSbO_4/Fe_2O_3$ ratios: these were 10 and 30 in $FeSbO_4$ CT1 and $FeSbO_4$ CT2, respectively.

The XRD patterns of the mechanical mixtures correspond to the superposition of those observed for the individual oxides. For the impregnated catalysts, patterns are those corresponding to the single impregnated $FeSbO_4$ cat-

Table 1
XPS Mo/Si, Fe/Si and Sb/Si atomic ratios for the impregnated $FeSbO_4$ CP1 with Mo ions

Catalyst	XPS Mo/Si			XPS Fe/Si			XPS Sb/Si		
	Fresh	Calcined	Used	Fresh	Calcined	Used	Fresh	Calcined	Used
$FeSbO_4$ CP1				0.33		0.30	0.44		0.450
$FeSbO_4$ CP1/0.25	0.11	0.10	0.10	0.22	0.25	0.22	0.29	0.37	0.37
$FeSbO_4$ CP1/1.50	0.18	0.16	0.15	0.23	0.25	0.21	0.32	0.40	0.37

alysts. No change was observed in the position or intensities of the peaks and no new peak was detected after reaction. No formation of a new phase was detected in $FeSbO_4$ CP1 impregnated with Mo ions after calcination.

3.1.4. XPS

An Sb enrichment on the surface is observed in pure $FeSbO_4$ catalysts. The XPS Fe/Sb atomic ratios are higher for the $FeSbO_4$ CP1, prepared by coprecipitation (Fe/Sb = 0.75) compared to those observed for $FeSbO_4$ obtained by the citrate method (Fe/Sb = 0.54 and 0.50 for $FeSbO_4$ CT1 and CT2, respectively).

For the mechanical mixtures, identical Fe/Si, Sb/Si and Mo/Si atomic ratios were observed in all cases before and after the test.

The XPS results concerning $FeSbO_4$ CP1 impregnated with Mo ions, with the lowest and the highest loading, are presented in Table 1. For fresh $FeSbO_4$ CP1 impregnated with Mo ions, an increase of the XPS Mo/Si atomic ratios is observed after Mo loading. After the test, or calcination, an increase of the Sb/Si atomic ratios and a slight decrease of the XPS Mo/Si atomic ratios are detected. The XPS Fe/Si increases after calcination and remains unchanged after the test.

Data for $FeSbO_4$ CT2 impregnated with Sb ions are shown in Table 2. Not all XPS atomic ratios are modified after the Sb loading. After the test, a decrease in the Fe/Si and in the Sb/Si atomic surface ratios and an increase in C/Si atomic ratio are detected. When the Sb content is high, the increase in C/Si is lower.

No change in the BE values of Sb3d3/2 (539.9 ± 0.2 eV) and Mo3d5/2 (233.1 ± 0.2 eV), Mo3d3/2 (235.8 ± 0.2 eV) was observed after the test or calcination.

3.2. Determination of the dispersion

Information about dispersion of MoO_3 and $\alpha\text{-}Sb_2O_4$ over $FeSbO_4$ was obtained by comparing the experimental XPS intensity ratios, $R_{\exp(\mathrm{Mo3d/Fe2p3})}$ and $R_{\exp(\mathrm{Sb3d3/Fe2p3})}$ with the theoretical values calculated according to the stacking monolayer (monoatomically dispersed supported phases) model proposed by Defossé [16]. The expected XPS intensity ratio, R_{sp}, is given by the relation: $R_{\mathrm{sp}} = \alpha dq$, where $\alpha = R'A\ R'L\ R'\sigma/C_{\mathrm{Fe}}\ \lambda_{\mathrm{Fe}})$. In this equation, $R'A = \phi_a/\phi_b$ [17], ϕ being the anisotropy parameter, $R'L = L_a/L_b$, where L is the analyzer luminosity calculated using the algorithm given by Weng

Table 2
XPS Fe/Sb, Fe/Si, Sb/Si and C/Si atomic ratios for the impregnated $FeSbO_4$ CT2 with Sb ions

Catalyst	XPS Fe/Sb		XPS Fe/Si		XPS Sb/Si		XPS C/Si	
	Fresh	Used	Fresh	Used	Fresh	Used	Fresh	Used
$FeSbO_4$ CT2	0.50	0.43	0.25	0.18	0.50	0.42	0.80	1.25
$FeSbO_4$ CT2/0.25	0.54	0.44	0.27	0.18	0.50	0.41	0.78	1.25
$FeSbO_4$ CT2/1.50	0.48	0.42	0.26	0.19	0.54	0.45	0.77	0.82

Table 3
Comparison of the XPS intensity ratios (R_{exp}) and those calculated using the stacking monolayer model of Defossé (R_{sp}) [16] for $FeSbO_4$ CP1 impregnated with Mo ions

$FeSbO_4$	$R_{exp(Mo3d/Fe2p3)}$			$R_{sp(Mo3d/Fe2p3)}$
impregnated with Mo	Fresh	Used	Calcined	
$FeSbO_4$ CP1/0.25	0.23	0.12	0.15	4.07
$FeSbO_4$ CP1/1.50	0.39	0.25	0.23	24.45

et al. [18] and $R'\sigma = \sigma_a/\sigma_b$, σ being the cross sections taken from the Scofield tables [19]. In the last three equations, a represents the Mo3d or Sb3d3 peaks and b represents the Fe2p3 peak. C_{Fe} is the volumetric atomic concentration of Fe in $FeSbO_4$ and λ_{Fe} is the electron free path which is determined using the algorithm given by Szajman et al. [20]. The surface density, d, is defined as $d = n_{Mo\ (or\ Sb)}/S_{BET}$, $n_{Mo\ (or\ Sb)}$ being the number of atoms of Mo (or Sb) per g of catalyst and S_{BET} the surface area of the support ($FeSbO_4$) in nm^2/g. Finally, q is a factor that depends only on the S_{BET} and turns close to 1 for low surface areas, as it does in our catalysts. The observed XPS intensity ratios are calculated from $R_{exp} = I_{Mo3d\ (or\ Sb3d3)}/I_{Fe2p3}$ where I is the peak intensity calculated from the relation, I = peak area × sensitivity factor. Results for $FeSbO_4$ CP1 impregnated with Mo ions are presented in Table 3. Clearly, the R_{sp} values are significantly higher than the R_{exp} values. When $FeSbO_4$ CT2 is impregnated with Sb ions, for $FeSbO_4$ CT2/0.25, $FeSbO_4$ CT2/0.5 and $FeSbO_4$ CT2/1.5, the $R_{sp(Sb3d3/Fe2p3)}$ values are 0.082, 0.165 and 0.495, respectively. The $R_{exp(Sb3d3/Fe2p3)}$ values, taking into account that the Sb signal includes both that of $FeSbO_4$ and of added Sb impregnated on $FeSbO_4$, are 0.74, 0.74, 0.87 and 0.94 for pure $FeSbO_4$ CT2, $FeSbO_4$ CT2/0.25, $FeSbO_4$ CT2/0.5 and $FeSbO_4$ CT2/1.5, respectively.

3.3. Catalytic tests

α-Sb_2O_4 is inert and MoO_3 shows a low activity with no formation of methacrolein. The results for the mechanical mixtures of both systems are presented in Table 4. $FeSbO_4$ prepared by the citrate method or coprecipitation is mainly active for complete oxidation with a low selectivity to methacrolein and produces large amounts of coke (catalysts are black after reaction).

Table 4
Catalytic results for $FeSbO_4$ CP1, $FeSbO_4$ CT1 and their mechanical mixtures (R_m = 0.5) with MoO_3 and α-Sb_2O_4

Sample	C%	R%	S%	CO_2%
$FeSbO_4$ CP1	31.0	7.0	22.5	26.5
$FeSbO_4$ CP1 + MoO_3	14.4	5.5	38.2	8.7
	(17.9)	(3.5)	(19.5)	(15.5)
	−19.0	**57.0**	**96.0**	**−44.0**
MoO_3	4.9	–	–	4.6
$FeSbO_4$ CT1	44.1	4.6	10.4	40.0
$FeSbO_4$ CT1 + α-Sb_2O_4	32.5	17.6	54.1	14.9
	(22.0)	(2.3)	(10.4)	(20.0)
	47.0	**665.0**	**420.0**	**−25.0**

In parentheses, theoretical values in absence of synergy, and in bold, synergy effect (see section 2.4). α-Sb_2O_4 is inert.

$FeSbO_4$ CP1 + MoO_3 shows a decrease in the conversion, a significant increase in the yield and in the selectivity to methacrolein and an important decrease in the CO_2 formation. $FeSbO_4$ CT1 + α-Sb_2O_4 shows an increase in the conversion, important synergetic effects in the yield and in the selectivity to methacrolein and a decrease in the CO_2 formation. Mixtures are not (or less) black after the tests.

Table 5 shows the catalytic results for the impregnated samples. The trends are similar to those observed with the mechanical mixtures. The principal effect when $FeSbO_4$ CP1 is impregnated with Mo ions or when $FeSbO_4$ CT2 is impregnated with Sb ions, is an important in-

Table 5
Catalytic results for impregnated samples: $FeSbO_4$ CP1 with Mo ions and $FeSbO_4$ CT2 with Sb ions

Sample	C%	R%	S%	CO_2%
$FeSbO_4$ CP1	32.0	7.5	23.3	21.1
$FeSbO_4$ CP1/1.50	20.6	10.0	48.8	10.4
$FeSbO_4$ CT2	46.0	7.2	15.6	38.8
$FeSbO_4$ CT2/1.50	32.0	16.1	50.3	16.0

crease in the yield and in the selectivity to methacrolein and a decrease in the CO_2 formation.

4. Discussion

4.1. Interpretation of the physicochemical results

XRD and BET do not give any indication of the formation of a new phase, even after the test in the mechanical mixtures. However, these are 'bulk techniques' and do not constitute conclusive proof to discard a possible spreading of Mo or Sb on the surface of $FeSbO_4$. The XPS results shed some light on these aspects. The fact that no change of XPS intensities is observed when mechanical mixtures were used in the catalytic reaction shows that there is no tendency of Mo to contaminate $FeSbO_4$. A very important finding concerns $FeSbO_4$ impregnated with Mo ions. XPS data, especially for $FeSbO_4$ CP1/1.50, indicate a decrease of the Mo/Si atomic ratio accompanied by a significant increase of the Sb/Si atomic ratio when the impregnated catalyst is calcined or used in the catalytic test (see Table 1). This shows that the impregnated ions have a tendency to detach from the $FeSbO_4$ surface. We admit that the variations are not dramatic, but the fact that our values are absolute, because they result from a comparison with an external standard (SiO_2) is a guarantee that we are dealing with a real effect.

The increase of the BET surface area after calcination or test is also an indication of that detachment. If our proposal is correct, a well-dispersed layer of MoO_3 (e.g., near monolayer), which does not add specific surface area to $FeSbO_4$, detaches to form small crystallites, that develop a new surface area, in addition to the one they leave free: this would indeed correspond to an increase of the BET surface area, as we observed. It thus seems that results point to an absence of contamination of $FeSbO_4$ by MoO_3 and even to a detachment of MoO_3 from the $FeSbO_4$ surface if MoO_3 is deliberately deposited on it. The main proof of the formation of small particles of MoO_3 on the surface of $FeSbO_4$ is given by the analysis of the dispersion (see section 3.2). It is clear that the values given by the model, $R_{sp(Mo3d/Fe2p3)}$, which are the values of the XPS atomic ratios that should be observed in the case of formation of a monolayer of Mo ions on the surface of $FeSbO_4$, are significantly higher compared to the XPS intensity obtained experimentally, $R_{exp(Mo3d/Fe2p3)}$. This provides evidence that the impregnated Mo ions sinterize and form small crystallites on the surface of $FeSbO_4$, drastically minimizing the initial artificial contamination on impregnated samples.

Unfortunately, the conclusions concerning a possible contamination of $FeSbO_4$ by Sb cannot be so clear, because the Sb signal includes both that of $FeSbO_4$ and of added Sb (α-Sb_2O_4 admixed with Sb impregnated on $FeSbO_4$). We can only assert that Sb from α-Sb_2O_4 does not form a large quantity of islands on $FeSbO_4$: if such a formation occurred, the Fe signal would diminish after the catalytic reaction. We did not observe such effect. On the contrary, the fact that an amount of Sb equivalent to 1.5 monolayer does not modify the intensity of the signal indicates that, in reality, α-Sb_2O_4 does not form a monolayer on $FeSbO_4$. The model of Defossé et al. [16] indicates a 503% increase of the Fe/Sb signal when the amount of impregnated Sb ions increases from the amount necessary to form 0.25 monolayer to that to form 1.5 monolayer, if such a monolayer was formed. On the contrary, for the same samples, the experimental values of Fe/Sb remain unchanged (Table 2). Approximate values of $R_{exp(Sb3d3/Fe2p3)}$ can be calculated by subtracting the intensity values corresponding to pure $FeSbO_4$ from the observed signal of $FeSbO_4/L$ values. In this case, the $R_{exp(Sb3d3/Fe2p3)}$ values increase by 8% for samples from $FeSbO_4$/0.5 to $FeSbO_4$/1.5, respectively. For the same samples, the model of Defossé indicates a 200% increase. It then seems that, account taken of the precision of the XPS calculations and measurements, we can state that if some tendency of Sb to contaminate $FeSbO_4$ exists, it is quite limited.

In conclusion, it seems logical to accept that both the mechanical mixtures and the impregnated $FeSbO_4$ catalysts are formed by the two oxide phases in good contact.

4.2. Interpretation of the catalytic results

Let us now consider the catalytic performances of the biphasic catalysts. The observed synergetic effects could have been explained by the formation of a new phase between MoO_3 or α-Sb_2O_4 and the excess Fe_2O_3, but this hypothesis can be discarded. In fact, it has been shown previously [7] that a pure Fe–Mo–O mixed phase, which is very active, but not selective, does not alone explain the increase in selectivity in the same reaction. On the contrary, in mixtures of Fe–Mo–O with α-Sb_2O_4 or MoO_3, important synergetic effects in the selectivity were observed. The deposition of small amounts of Mo or Sb ions on the surface of $FeSbO_4$ considerably modifies its catalytic properties. The yield in methacrolein is significantly increased. A small quantity of Sb ions (the nominal loading which would be necessary to form about 1.5 monolayers, but actually forms small crystallites) is sufficient to increase the yield by 124%. In the case of Mo ions, the increase is 33%. In mechanical mixtures also, the synergetic effects on the yield and on the selectivity in methacrolein are spectacular.

Physicochemical characterization results support the conclusion that the synergetic effects observed are due to a large extent, possibly conclusively, to a cooperation between well individualized phases, namely $FeSbO_4$ on the one hand and MoO_3 or α-Sb_2O_4 on the other. This could correspond to a remote control mechanism. The exact role of $FeSbO_4$ will depend on the oxide (MoO_3 or α-Sb_2O_4) with which it is contacted.

(1) When $FeSbO_4$ is mixed with MoO_3 the selectivity is higher. The same effect is observed when donors, such as α-Sb_2O_4, $BiPO_4$, Cu-doped α-Sb_2O_4 [5,6,21,22], are mixed with MoO_3. This can be explained by the action of the (small) flux of O_{so} from $FeSbO_4$ which reoxidizes reduced sites on the surface of MoO_3 more efficiently. This increases the number of selective sites and inhibits the non-selective ones. $FeSbO_4$ thus act as a donor. During the oxidation of isobutene on MoO_3, a surface oxidoreduction cycle with a continuous alternation of edge-sharing and corner-sharing arrangements occurs. In the absence of O_{so} (pure MoO_3), the proportion of edge-sharing groups tends to increase because reoxidation by O_2 is slightly slower than the removal of oxygen by the hydrocarbon.

In conclusion, in this case $FeSbO_4$ contributes strongly to the selective reaction, and produces spillover species that migrate onto the surface of MoO_3, increasing the number of selective sites and inhibiting the non-selective ones.

(2) Let us consider now the case of $FeSbO_4$ mixed with α-Sb_2O_4. It is very likely that the oxidation of isobutene on pure $FeSbO_4$ is accompanied by some surface reduction resulting in a non-selective catalyst. The reoxidation of reduced sites is the rate-limiting step. Pure $FeSbO_4$ is unable to reoxidize the reduced sites by using molecular oxygen efficiently, or through a migration of lattice oxygen from its bulk, because the migration would be slow compared with the consumption of oxygen on the surface; but in the biphasic catalysts, O_{so} produced by α-Sb_2O_4 probably inhibits (thanks to reoxidation) the formation of non-selective sites, thus maintaining selectivity and explaining the increase in methacrolein formation. The fact that there also is an increase in the conversion of isobutene is interesting, confirming that O_{so} regenerates deactivated sites on $FeSbO_4$.

We therefore propose that the main explanation for the better performance of $FeSbO_4$ covered by a layer of α-Sb_2O_4 is the occurrence of an RMC (cooperation of $FeSbO_4$ and α-Sb_2O_4).

Results on impregnated samples support this assessment. Recent results [23] show that $FeSbO_4$ with stoichiometric Fe/Sb atomic ratio is very active, but completely unselective. Only total oxidation products and coke formation were observed. The same $FeSbO_4$ increases its selectivity to methacrolein when mixed mechanically with a small amount of α-Sb_2O_4, confirming that 'enriched $FeSbO_4$' acts as a two-phase catalyst. This result also suggests that the donor role played by $FeSbO_4$ in the present experiments is not due to $FeSbO_4$ itself, but rather to the presence of an excess of antimony on the surface or, more specifically, to small crystallites of α-Sb_2O_4 particles segregated during calcination of the catalysts.

It has also been shown that O_{so} can inhibit the deposition of coke by burning out either its precursors or the coke itself. This could explain why the biphasic catalysts, $FeSbO_4$ + α-Sb_2O_4, are not black after the tests. Similar results have been observed with other oxides in previous investigations [5,6,8,9,13,21,22].

5. Conclusions

A cooperative effect is observed between $FeSbO_4$, probably somewhat enriched with Sb on the one hand, and MoO_3 or α-Sb_2O_4 on the other hand, in the oxidation of isobutene. This can be explained by the remote control mechanism. It is proposed that $FeSbO_4$ is a donor of oxygen spillover when it is mixed with MoO_3, and an acceptor in presence of α-Sb_2O_4.

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