Catalytic Performances and Stability of Three Sb-Mo-O Phases in the Selective Oxidation of Isobutene to Methacrolein

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We investigated the possible role of binary oxides associating Sb and Mo in the synergetic effects between physically mixed MoO₃ and α -Sb₂O₄ in the selective oxidation of isobutene to methacrolein. The catalytic behavior of three Sb-Mo-O phases-Sb₂MoO₆ on one hand, a mixture of $Sb_2Mo_{10}O_{31}$ and $Sb_4Mo_{10}O_{31}$ on the other hand—was investigated. The samples were characterized using X-ray diffraction (XRD), confocal laser Raman microscopy, specific area measurements, and scanning electron microscopy. Additional in situ high-temperature XRD was also performed. At similar conversions of isobutene, the selectivities to methacrolein for the Sb-Mo-O phases were always lower than those of mixtures of MoO₃ with α -Sb₂O₄ with the same atomic compositions. A second result was that the three Sb-Mo-O phases were unstable in the conditions of reaction and tended to decompose to simple molybdenum and antimony oxides. An improvement of the catalytic performances of the Sb-Mo-O catalysts occurred in parallel to their decomposition. Some apparent cooperation effects were observed for mechanical mixtures of the Sb-Mo-O phases with MoO₃ or α -Sb₂O₄. These effects are actually related to the decomposition of the Sb-Mo-O phases and are due to the cooperation between MoO₃ and α -Sb₂O₄ formed at their surface. The spontaneous decomposition of the Sb-Mo-O phases shows that these phases cannot form in operandi (during the catalytic reaction) starting from the simple oxides. Consequently, this shows that they cannot be the real most performant phases in the mixtures of MoO₃ with α -Sb₂O₄ and hence that they cannot be at the origin of the synergism between the simple oxides.

1. Introduction

A conspicuously strong cooperation effect was found in the selective oxidation of isobutene to methacrolein when using an MoO₃ sample developing preferentially the (010) faces mechanically mixed with α -Sb₂O₄. Synergetic enhancements of both the isobutene conversion and the selectivity to methacrolein were observed showing that new selective sites had been created at the surface of MoO_3 in the presence of α -Sb₂O₄. The phenomenon was explained by the occurrence of a remote control mechanism between the two oxides. According to this mechanism, α -Sb₂O₄ irrigates the catalyst with spillover oxygen. This reacts with the surface of MoO₃ crystals where it induces the facetting of the nonselective (010) faces to more active and more selective (100) steps. As strongly suggested by the characterization of the catalysts after reaction, the model applied adequately because the two oxides incorporated in the mixture remained completely separate during the catalytic reaction and because there was no evidence of mutual contamination. However, when comparing carefully the XRD patterns of the mixture before and after catalysis, some faint indications led us to wonder whether a phase containing Sb, Mo, and O simultaneously, in particular Sb₂Mo₁₀O₃₁, could have been formed in a small amount during the reaction and hence could

contribute to the synergetic effects observed.^{1,2} The main objective of the experiments presented here was to evaluate the role that such binary phase, if really formed, could play in the improvement of the performances observed for the mixtures of MoO₃ with α -Sb₂O₄.

Weng and Delmon listed the different possible origins of the synergetic effects between physically mixed simple phases.³ Among these, the formation of binary phases during the reaction has been frequently cited. On one hand, a new phase could present performances higher than those of the starting simple oxides in the mixture. On the other hand, even if formed in small amount, the new phase could cover the surface of the starting material and hence could extensively influence the overall activity of the catalyst. Enhancement of the performances would thus be obtained. The reaction of Bi2O3 with MoO₃ to form Bi-Mo-O binary compounds constitutes a classical example of the formation of a more active and more selective new phase.⁴ In principle, this line of interpretation could be extended to other types of mutual contaminations, like solid solutions and surface contamination layers formed from the simple oxides.³ In addition to this, and even if it is not directly evoked in the review of Weng and Delmon,³ one could also imagine another situation where a binary phase could play a beneficial role on the performances of the catalyst by a mechanism other than by exerting its own activity. Starting from a mixture of simple oxides, this would be the formation of a possibly inactive and/or nonselective binary phase during the catalytic reaction, which could thus not be directly respon-

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sible for the enhanced performances of the mixture but which could cooperate with one (or more) of the remaining nontransformed initial simple oxides. In this case, the improvement of the performances would be due to this cooperation. This situation is mechanistically equivalent to that where synergisms were detected for mixtures containing a simple oxide and an oxide phase containing several metals.^{5–8} The only difference is that the binary phase would form *in operandi* rather than being synthesized separately and mixed with the simple oxides afterward.

In the case of the mixtures of MoO₃ with α -Sb₂O₄, extensive investigations have been carried out in order to evaluate the possibility to form binary oxides or contamination phases (solid solutions or surface contamination layers) and to measure their stability under the conditions of catalytic oxidation reactions. It was shown that surface contamination layers of Sb ions on MoO₃ or of Mo ions on α -Sb₂O₄ did not form in the catalytic conditions. On the contrary, when prepared artificially, these layers were unstable and their transformation led to a decontamination under the reaction conditions, namely the breaking of the layer and its sintering to crystallites.^{3,9–13} The situation was similar when considering the formation of bulk mixed phases containing Sb, Mo, and O simultaneously. Except for the work mentioned before using a mixture containing (010)oriented MoO₃,¹ the formation of a Sb–Mo–O phase was never detected in the used mixtures of MoO₃ and α -Sb₂O₄. Attempts to synthesize a binary phase by coprecipitation of molybdenum and antimony salts or by solid-state reactions of MoO3 and α -Sb₂O₄ were unsuccessful.^{9,14,15} But the evaluation of the stability of these phases in the catalytic conditions was never undertaken experimentally. Weng et al. considered that it was almost certain that they would decompose during catalytic selective oxidation.^{3,9} Their conclusion was based on the work of Parmentier et al.¹⁶⁻¹⁹ These authors reported (i) that the preparation of the Sb-Mo-O phases requires conditions that are far from those of the catalytic activity measurements (for Sb₂MoO₆, calcination at 500 °C in reduced pressure of argon; for Sb₂Mo₁₀O₃₁ or Sb₄Mo₁₀O₃₁, calcination around 500 °C in nitrogen with a small amount of hydrogen in the presence of high concentrations of water) and (ii) that the Sb-Mo-O phases decompose spontaneously in air between 350 and 400 °C. The criticism against the argumentation of Weng et al. would be that the gas mixture used for the catalytic reaction, even if presenting a composition closer to air than to hydrogen diluted in nitrogen, in particular presenting an almost identical concentration in oxygen, also contained 10% of isobutene. It is very difficult to evaluate the extent to which isobutene would maintain the atmosphere in the reactor reductive enough to allow the formation of a Sb-Mo-O phase. The main difficulty in this evaluation is that the reductive potential is actually determined by the dynamics of the reduction-oxidation cycle to which the surface of the solid is subjected, and not by the overall static value obtained through a traditional thermodynamic evaluation. The assumption of Weng et al. that Sb-Mo-O phases could not form must therefore be reexamined, and this, experimentally.

To give a clear view of the role(s) of the Sb–Mo–O phases in the synergetic effects measured in the selective oxidation of isobutene to methacrolein for mixtures of MoO₃ with α -Sb₂O₄, three main experimental lines were followed. (i) Determination of the extent to which the own reactivity of the Sb–Mo–O phases could explain the higher performances observed for the mixtures of MoO₃ with α -Sb₂O₄. This consisted in comparing the catalytic performances of the binary phases under appropriate conditions with those of mixtures of simple oxides with comparable compositions. (ii) Evaluation of the extent to which a cooperation between the Sb-Mo-O phases and simple MoO₃ or α -Sb₂O₄ could take place. The approach followed was that classically used for the detection of the catalytic cooperations between separate phases, namely, comparing the catalytic performances of mechanical mixtures of a Sb-Mo-O phase with MoO₃, or with α -Sb₂O₄, with those of the constituting phases tested individually. (iii) Evaluation of the stability of the Sb-Mo-O phases in the conditions of reaction. This consisted in observing the evolution with time on stream of the performances of the Sb-Mo-O phases and in characterizing them before and after catalytic tests with different durations using X-ray diffraction, confocal laser Raman microscopy, scanning electron microscopy, and specific area measurements. In situ X-ray diffraction performed in the presence of air in a high-temperature cell was also carried out for this purpose.

Although only Sb₂Mo₁₀O₃₁ was suspected to form in the mixtures of MoO₃ with α -Sb₂O₄, we investigated additionally Sb₂MoO₆ and Sb₄Mo₁₀O₃₁. Sb₂MoO₆ is a molybdate with a monoclinic crystallographic symmetry. In Sb₂Mo₁₀O₃₁ and Sb₄Mo₁₀O₃₁, crystallized in orthorombic and hexagonal symmetries, respectively, the average experimental oxidation levels of Mo are 5.44 and 5.06.^{16–19}

The performances of the catalysts reported in what follows, in particular their selectivities to methacrolein, are low compared to those of actual industrial catalysts used for the selective oxidation of isobutene. As an example the formulation proposed by Blangenois et al. leads to a selectivity to methacrolein higher than 90%, while those of the catalysts studied here only reach 47% at the maximum.²⁰ One could wonder about the significance and the interest, at the industrial point of view, of an investigation on catalysts such as in this contribution. As an answer, we have to mention that our objective is not to challenge the existing industrial catalysts. Commercial catalysts for selective oxidation reaction of isobutene or similar are often composed of intimately mixed Sb and Mo. Our objective is to throw light on the way the combination of these two elements can bring about improvement of performances, precisely to clarify whether they do so by being associated in a mixed oxide or, on the contrary, by remaining in two separate simple oxide phases-which is a very controversial point. Our strategy has been to study model catalysts with architectures as controlled as possible to make the interpretation of their performances as simple as possible: single Sb-Mo-O phases and mechanical mixtures of simple oxides were selected. This choice was made at the detriment of possibly higher catalytic performances of catalysts with less defined structures. Nevertheless, all the conclusions drawn in the present study can be directly transposed for a better understanding of the working mechanism of the real industrial catalysts. This fully justifies the interest to carry out this investigation.

2. Experimental Section

2.1. Preparation of the Catalysts. *2.1.1. Preparation of the Sb–Mo–O Phases.* Three phases containing Sb, Mo and O simultaneously have been synthesized by solid-state reactions following the procedures described by Parmentier et al.^{16–19}

2.1.1.1. Sb_2MoO_6 . Commercial Sb_2O_3 (14.475 g, Janssen Chimica, 99+%) was ground in an agate mortar with commercial MoO₃ (7.197 g, BDH Chemicals, 99.5+%) in a 1:1 molar ratio. To maintain the stoichiometry of the system unchanged, namely, to avoid any O supply from the atmosphere



Figure 1. XRD pattern ($\lambda = 1.5418$ Å, step size = 0.04°, step time = 6 s) of Sb₂MoO₆; the asterisks * indicate the positions of the standard reflection lines of this phase (file 33-1491 JCPDS²¹).

and to avoid any O and Mo loss due to MoO_3 sublimation during the synthesis, the mixture was evacuated in a glass tube down to 10^{-4} mbar. The tube was then filled with 670 mbar of Ar, sealed, and thereafter maintained at 500 °C for 24 h.

The X-ray diffraction (XRD) pattern of the resulting orange powder presented all the reflection lines with relative intensities as listed in the Sb₂MoO₆ standard 33-1491 JCPDS file.²¹ No other line was present. In particular, no line corresponding (i) to nonreacted MoO₃, or any other molybdenum oxide or suboxide possibly formed during the synthesis, (ii) to nonreacted Sb₂O₃, or (iii) to any other Sb, Mo and O-containing phases listed in the JCPDS database, was detected.²¹ Figure 1 presents the XRD pattern of the Sb₂MoO₆ sample. The specific area developed by Sb₂MoO₆ was 0.38 m² g⁻¹.

2.1.1.2. Sb₂Mo₁₀O₃₁ and Sb₄Mo₁₀O₃₁. Sb₂Mo₁₀O₃₁ was synthesized starting from a mixture of Sb₂MoO₆ (3.774 g, prepared as described before) and MoO₃ (11.227 g, BDH Chemicals, 99.5+%) with a 1:9 molar ratio. The mixture was heated at 10 °C min⁻¹ to 520 °C in N₂ (Air Liquide, 99.8%) and thereafter maintained at the same temperature under a flowing (50 mL min⁻¹) H₂/N₂ mixture (1/99 vol.), saturated with 570 mmHg of water (corresponding to the water vapor pressure in equilibrium with liquid water at 92 °C). The system was afterward cooled in N_2 . The high proportion of H_2O with respect to H_2 in the preparation atmosphere was fixed so that the global reductive potential of the system was tuned at a very low value and allowed to trigger the mild reduction of Mo required for the formation of the binary phase. To complete the reaction, the obtained solid was finely ground and submitted to a second calcination cycle following the same procedure.

Purple flakes were obtained. XRD analysis showed that $Sb_2Mo_{10}O_{31}$ (JCPDS standard file 33-0105) was the main crystallographic phase formed. Some $Sb_4Mo_{10}O_{31}$ (JCPDS standard file 33-0104) was also present.²¹ No other crystalline Sb-Mo-O mixed phase was detected, but small amounts of several MoO_{3-x} phases were found. This is logical considering that Sb got incorporated in the Mo-poor $Sb_4Mo_{10}O_{31}$ phase rather than in the desired $Sb_2Mo_{10}O_{31}$ Mo-rich one. The Mo excess resulting from this effect led to the formation of MoO_{3-x} phases in small amounts.

Attempts to prepare Sb₂Mo₁₀O₃₁ or, alternatively, Sb₄Mo₁₀O₃₁ (following the same procedure as for Sb₂Mo₁₀O₃₁, but starting from a mixture of Sb₂MoO₆ with MoO₃ in a 1:4 molar ratio and fixing the calcination temperature at 500 °C and the water vapor pressure at 532 mmHg) with higher purities were unsuccessful. The investigation of the catalytic behavior of Sb₂Mo₁₀O₃₁ and Sb₄Mo₁₀O₃₁ was therefore made simultaneously



Figure 2. XRD pattern ($\lambda = 1.5418$ Å, step size = 0.04°, step time = 6 s) of "Sb_mMo₁₀O₃₁"; the positions of the standard reflection lines of Sb₂Mo₁₀O₃₁ (JCPDS file 33-0105) and of Sb₄Mo₁₀O₃₁ (JCPDS file 33-0104) are indicated with the asterisks * and circles O, respectively.²¹

 TABLE 1: Compositions (in wt %) of the Mechanical Mixtures Prepared

mixture	phase 1	phase 2	proportions (wt %)
1 2 3 4	$\begin{array}{c} Sb_2MoO_6\\Sb_2MoO_6\\Sb_mMo_{10}O_{31}\\Sb_mMo_{10}O_{31}\end{array}$	$\begin{array}{c} MoO_3\\ \alpha-Sb_2O_4\\ MoO_3\\ \alpha-Sb_2O_4 \end{array}$	50/50 50/50 50/50 50/50
5 6 7	MoO ₃ MoO ₃ MoO ₃	$\begin{array}{l} \alpha \text{-} Sb_2O_4 \\ \alpha \text{-} Sb_2O_4 \\ \alpha \text{-} Sb_2O_4 \end{array}$	25/75 50/50 75/25

using the sample synthesized as described before, hereafter noted "Sb_mMo₁₀O₃₁". Figure 2 shows the XRD pattern of Sb_mMo₁₀O₃₁. Sb_mMo₁₀O₃₁ developed an 0.17 m² g⁻¹ specific area.

2.1.2. Preparation of Simple Oxides: Molybdenum Trioxide and Antimony Oxide. MoO₃ was prepared by calcination in air of ammonium heptamolybdate tetrahydrate (Merck, p.a.) at 500 °C over 20 h; α -Sb₂O₄ was synthesized in the same conditions starting from Sb₂O₃ (UCB Chemicals, p.a.). XRD analysis showed that the obtained samples were, respectively, pure molybdite (JCPDS standard file 05-0508) and cervantite (JCPDS standard file 11-0694) crystallographic phases, respectively.²¹ The specific areas of MoO₃ and α -Sb₂O₄ were 0.48 and 0.50 m² g⁻¹, respectively.

2.1.3. Preparation of Mechanical Mixtures. "Mechanical mixtures", also called "physical mixtures" in this paper, were prepared by vigorously mixing a suspension in *n*-pentane of adequate amounts of powders synthesized as described above. Ultra-Turrax agitation was applied for 10 min at 6000 rpm. Afterward, the interdispersion of the phases was completed ultrasonically over 10 min. The *n*-pentane was then removed under vacuum at room temperature before the remaining solid was dried gently in air at 80 °C overnight. Table 1 lists all the mechanical mixtures prepared. Two series can be distinguished: (i) mixtures of a binary Sb–Mo–O phase with a simple oxide (mixtures 1 to 4), (ii) mixtures of two simple oxides (mixtures 5 to 7). To compare rigorously the performances of the mixtures with those of the pure phases, these were submitted to exactly the same "mixing" procedure before being catalytically tested.

An X-ray diffraction analysis was done before the catalytic test. The patterns obtained for the pure phases having been submitted to the mechanical mixture procedure never showed any difference with those of the corresponding "nonmixed" samples. Also, the patterns of the mixtures corresponded perfectly to the theoretical patterns reconstituted by the simple ponderated addition of those measured for the pure constituting phases.

2.2. Catalytic Activity Measurements. In the absence of special indication (about reaction temperature, mass of catalyst tested, or duration of reaction) in the following, catalytic tests were carried out in what is described hereafter as the "classical conditions". The isobutene oxidation was performed in a fixed bed reactor at 420 °C. The composition of the gas mixture was isobutene/O₂/He = 1/2/7 vol. The total gas flow was 30 mL min^{-1} . The mass of catalyst tested was 500 mg. The samples were used as powders without pressing them into pellets and were diluted in an equal volume of small glass balls (0.49 mm < diameter < 0.72 mm) previously checked to be inactive. The unreacted isobutene and the methacrolein produced were analyzed by on-line gas chromatography. For all the catalytic tests shown after, CO₂-a derivative of isobutene and/or of methacrolein through a total oxidation process-was the only product detected in addition to methacrolein: no other partially oxygenated derivatives of isobutene or of methacrolein (alcohols, aldehydes, ketones, or carboxylic acids) nor other deep or total oxidation products (e.g., formic acid or CO) were dectected. After 3 h of reaction, the catalysts were cooled to room temperature at a rate of 7.5 °C min⁻¹ in the same flow as during the reaction. Catalytic performances were expressed in terms of isobutene conversion (%C) and yield and selectivity to methacrolein (%Y(meth) and %S(meth), respectively). For reasons of clarity, and because the investigation of the mechanism of its formation was not the main point of our discussion, we did not report the yield and selectivity to CO₂. However as being the only other product of reaction than methacrolein, the selectivity to CO_2 is the complement to %S(meth) to reach a 100% selectivity. Following the basic recommendations dealing with the kinetics of consecutive reactions, the comparison of selectivities to methacrolein on the different catalysts was done at comparable low conversion of isobutene. The comparison of the conversion of isobutene and yield to methacrolein was made after normalizing the measured values to the surface (expressed in m²) developed by the mass of catalyst used for the tests. In the following, we call these normalized values "intrinsic conversion and yield". When necessary, an "intrinsic selectivity" was calculated by reporting the intrinsic yield to the intrinsic conversion.

Attention was directed to the comparison of the catalytic performances of the Sb-Mo-O phases with those of mixtures of MoO₃ with α -Sb₂O₄. Potentially, Sb₂MoO₆ contacted with O_2 could decompose to a mixture of MoO₃ and α -Sb₂O₄ with a composition close to the mechanical mixture containing 25 wt % of MoO₃ and 75 wt % of α -Sb₂O₄. This was selected for the comparison with Sb₂MoO₆. Similarly, the performances of the $Sb_mMo_{10}O_{31}$ sample were compared with those of the mixture containing 75 wt % of MoO₃ and 25 wt % of α -Sb₂O₄. To reach conversions of isobutene similar to those on the binary phases, the masses of mixtures of MoO₃ with α -Sb₂O₄ tested were adapted from 500 mg (corresponding to the "classical conditions") to 400 mg. For this section, the performances reported correspond to the values measured immediately when the reactor stabilized at 420 °C-we called them "initial performances".

Another objective was to explore the stability of the Sb– Mo–O phases during the catalytic reaction. Attention was particularly directed to the evolution of their catalytic performances as a function of the time on stream. In addition to the tests performed in the "classical conditions", the pure Sb– Mo–O phases were tested at 450 °C over 14 h (for Sb₂MoO₆ and Sb_mMo₁₀O₃₁) and over 8 days (for Sb_mMo₁₀O₃₁ only). In both cases, the reaction at 450 °C was preceded and followed by catalytic activity measurements at 420 °C—for these experiments, the performances at 420 °C correspond to the initial values measured immediately after the reactor stabilized at this temperature.

The performances of the mixtures of the binary Sb–Mo–O phases with the simple oxides were also measured under the classical conditions in order to detect possible synergetic effects. For that purpose, the performances measured were compared with theoretical values calculated on the basis of the performances obtained when the phases constituting the mixture were tested individually and assuming that the phases in the mixture behaved independently without any cooperation (eqs 1). The performances reported for this section correspond to the values arithmetically averaged on the totality of the 3 h of test.

 $%C_{th} = [%C \text{ obtained with A} \times$

mass fraction of A in the mixture] +

[%C obtained with $B \times mass$ fraction of B in the mixture]

theoretical yield in methacrolein:

 $%Y_{th}(meth) = [%Y(meth) obtained with A \times$

mass fraction of A in the mixture] +

[% Y(meth) obtained with B \times

mass fraction of B in the mixture]

(1b)

(1c)

theoretical selectivity to methacrolein:

 $%S_{th}(meth) = Y_{th}(meth)/\%C_{th} \times 100$

2.3. Characterization. The catalysts were characterized before and after the catalytic tests by X-ray diffractometry (XRD) on a Kristalloflex Siemens D-5000 equipment. Analyses were carried out in the continuous coupled $\theta/2\theta$ scan reflection mode using the K $\alpha_{1,2}$ radiation of Cu ($\lambda = 1.5418$ Å) for 2θ angles varying from 10 to 80°. The fluorescence contribution was eliminated from the diffracted beam using a curved graphite monochromator. The scan rate was 0.4 deg min⁻¹ with a step size of 0.04° and a step time of 6 s.

Additional XRD measurements were performed at high temperature in an in situ XRD cell interfaced with an HTK 10 High Temperature Attachment. Analyses were done in air with the same parameters as described above. Two analysis sequences were realized focusing (i) on the evolution of the XRD pattern as a function of the temperature and (ii) on the evolution of the XRD pattern at 420 °C as a function of time, respectively. For cycle i, XRD patterns were measured consecutively at 30, 200, 300, 400, 500, and 600 °C and again at 30 °C. The temperature set for the analysis was reached with a rate of 1 °C s⁻¹. The sample was maintained at the analysis temperature during 1 h before the recording of the pattern started. The total time of analysis for cycle i was 22.5 h. Cycle ii consisted of a first measurement of the XRD pattern of the sample at 30 °C followed by seven consecutive measurements at 420 °C and an additional analysis at 30 °C. No time delay was introduced in the sequence between the moment the analysis temperature was reached and the beginning of the pattern measurement. The total time of analysis for cycle ii was 19.8 h. The two cycles were applied to Sb₂MoO₆, to Sb_mMo₁₀O₃₁ and to their mechanical mixtures with α -Sb₂O₄.

For both types of XRD analyses, only the results obtained with the pure Sb, Mo, and O-containing phases are presented and discussed hereafter. The interpretation of the results with

TABLE 2: Comparison, at Comparable Small Conversion of Isobutene, of the Selectivity to Methacrolein at 420 °C on the Sb–Mo–O Phases (Initial Performances) and the Corresponding Mixtures of MoO₃ with α -Sb₂O₄

catalyst	mass tested, mg	%C	%Y (meth)	%S (meth)
Sb ₂ MoO ₆	500	4.3	0.0	0.0
$MoO_3 + \alpha - Sb_2O_4 25/75$ (wt %)	400	7.2	3.3	45.4
$Sb_mMo_{10}O_{31}$	500	4.2	0.6	13.7
$MoO_3 + \alpha - Sb_2O_4 75/25$ (wt %)	400	5.9	1.5	25.2

the mixtures was impossible because of the simultaneous presence of several phases in the samples with most of the peaks overlapping, and because of the much higher crystallinities of the simple oxides compared to those of the Sb–Mo–O phases (whose peaks were masked by the intense reflections of the simple oxides).

Confocal laser Raman microscopy was performed with a Dilor Labram I spectrometer equipped with a computerized X-Y translation stage. The analysis was made on the Sb-Mo-O phases before and after tests over 14 h at 450 °C. The Raman spectra were excited using a He laser (632.8 nm, Melles Griot) operated at 15 mW power. The spectrometer resolution was 2 cm^{-1} . A notch filter was applied to cut off the laser line and the Rayleigh scattering up to 100 cm^{-1} . The spectrometer was equipped with a CCD detector (1024×298 diodes), which was Peltier-cooled to 240 K in order to reduce thermal noise. Though the spectrometer function and the characteristics of the diode array are unknown, it was assumed that the recorded spectra (band positions and band profiles) really represented the sample. For each sample, Raman spectra were recorded using the scanning multichannel technique (SMT) at about 750 different spots (i.e., 30 spots \times 25 spots) regularly dispersed in a sample area of $40 \times 30 \,\mu\text{m}^2$. The spatial resolution of each spot was approximately 0.7 μ m. This technique gives a complete picture of the composition of the samples. The spectra shown hereafter have been checked not to be perturbed by the occurrence of a thermal degradation of the samples under the laser beam during the analysis. In the discussion of the LRS spectra, the objective was not to assign exhaustively all the bands of the spectra, but we mainly focused on the interpretation of the differences between the spectra measured for the corresponding samples before and after the catalytic reaction.

Specific area measurements SBET were performed on the Sb–Mo–O phases after the catalytic tests during 14 h at 450 °C using a Micromeritics ASAP 2000 device. The analysis was based on the adsorption of Kr at the liquid nitrogen temperature.

Scanning electron microscopy (SEM) was performed on a Hitachi S-570 microscope using a 15 kV accelerating voltage. We checked the occurrence of the presented features in many different places so that all the SEM micrographs shown hereafter are representative of the whole samples. Analysis was made on Sb₂MoO₆, fresh and after test at 450 °C, and on Sb_mMo₁₀O₃₁, fresh, after test at 420 °C, after test at 450 °C over 14 h, and after test at 450 °C over 8 days.

3. Results

3.1. Catalytic Activity Measurements. 3.1.1. Activity at 420 °C of the Sb-Mo-O Phases-Comparison with the Mechanical Mixtures of MoO₃ with α -Sb₂O₄. Table 2 compares the initial selectivity to methacrolein at similar low conversion of isobutene obtained at 420 °C on the binary Sb-Mo-O phases and on the mixtures of MoO₃ with α -Sb₂O₄ with comparable atomic compositions. Table 3 compares the intrinsic conversion of isobutene and the intrinsic yield to methacrolein for the two

TABLE 3: Comparison of the Intrinsic Conversion of Isobutene and Intrinsic Yield to Methacrolein at 420 °C on the Sb–Mo–O Phases (Initial Performances) and the Corresponding Mixtures of MoO₃ with α -Sb₂O₄

catalyst	$%C m^{-2}$	% Y(meth) m ⁻²
Sb ₂ MoO ₆	22.4	0.0
$MoO_3 + \alpha - Sb_2O_4 25/75 \text{ (wt \%)}$	36.2	16.4
$Sb_mMo_{10}O_{31}$	49.4	6.7
$MoO_3 + \alpha - Sb_2O_4 75/25 \text{ (wt \%)}$	30.5	7.7
5,5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5	← %C (Sb2)	MoO6) MoI0031)
0 20 40 60 80	0 100 120	0 140 160

Figure 3. Evolution with time of the conversion of isobutene at 420 °C on Sb_2MOO_6 and $Sb_mMO_{10}O_{31}$.

Time (min)



Figure 4. Evolution with time of the selectivity to methacrolein at 420 °C on Sb_2MoO_6 and $Sb_mMo_{10}O_{31}$.



Figure 5. Evolution with time of the conversion of isobutene at 450 °C on Sb_2MoO_6 and $Sb_mMo_{10}O_{31}$.

series of catalysts. On one hand, Sb₂MoO₆ presented a lower intrinsic conversion of isobutene than the corresponding mixture of MoO₃ with α -Sb₂O₄, but Sb_mMo₁₀O₃₁ was intrinsically more active than its comparable mixture of simple oxides (Table 3). On the other hand, both Sb-Mo-O phases exhibited lower selectivities to methacrolein than the mixtures of MoO₃ with α -Sb₂O₄ (Table 2).

3.1.2. Evolution of the Catalytic Performances of Sb-Mo-OPhases with the Time on Stream. Figures 3 and 4 show the evolution with time on stream of the isobutene conversion and selectivity to methacrolein at 420 °C for Sb_2MoO_6 and $Sb_mMo_{10}O_{31}$. Figure 5 gives the same information for the conversion in the tests performed at 450 °C over 14 h. Table 4 compares the selectivity to methacrolein obtained at 420 °C

TABLE 4: Comparison, at Comparable Small Conversion of Isobutene, of the Selectivity to Methacrolein at 420 $^\circ C$ on the Sb–Mo–O Phases Before and After Catalytic Reaction at 450 $^\circ C$ for 14 h

catalyst		%C	%Y(meth)	%S(meth)
Sb ₂ MoO ₆	before 450 °C	3.3	0.6	17.1
	after 450 °C	5.6	1.4	24.4
$Sb_mMo_{10}O_{31}$	before 450 °C	3.7	0.6	17.7
	after 450 °C	3.2	0.7	22.0

TABLE 5: Comparison of Intrinsic Conversion of Isobutene and Intrinsic Yield to Methacrolein at 420 $^\circ$ C on the Sb–Mo–O Phases Before and After Catalytic Reaction at 450 $^\circ$ C 14 h

catalyst		$\%C m^{-2}$	$% Y(meth) m^{-2}$
Sb ₂ MoO ₆	before 450 °C	17.3	3.0
	after 450 °C	41.2	10.1
$Sb_mMo_{10}O_{31}$	before 450 °C	43.1	7.6
	after 450 °C	18.5	4.1

TABLE 6: Observed and Theoretical Conversion of Isobutene, Yield, and Selectivity to Methacrolein on the Mixtures of Sb-Mo-O Phases with Simple Oxides at 420 $^{\circ}C^{a}$

catalyst	%C	%Y(meth)	%S(meth)
Sb ₂ MoO ₆	4.6	0.6	12.5
$Sb_mMo_{10}O_{31}$	4.6	0.7	14.7
MoO ₃	5.3	0.4	6.7
α -Sb ₂ O ₄	2.4	0.0	0.0
Sb ₂ MoO ₆ + MoO ₃ 50/50 (wt %)	5.3 (4.9)	1.2 (0.5)	22.1 (9.4)
$Sb_2MoO_6 + \alpha - Sb_2O_4 \ 50/50 \ (wt \ \%)$	4.1 (3.5)	0.9 (0.3)	22.7 (8.3)
Sb _m Mo ₁₀ O ₃₁ + MoO ₃ 50/50 (wt %)	4.2 (4.9)	0.6 (0.5)	14.2 (10.4)
$Sb_mMo_{10}O_{31} + \alpha - Sb_2O_4 50/50 \text{ (wt \%)}$	4.5 (3.5)	0.7 (0.3)	14.7 (9.8)
$MoO_3 + \alpha - Sb_2O_4 50/50 \text{ (wt \%)}$	6.5 (3.8)	3.0 (0.2)	46.7 (4.6)

^{*a*} The theoretical values (in parentheses) were calculated, assuming the absence of cooperation, on the basis of the mass-ponderated conversions and yields to methacrolein of the pure phases tested alone (see eq 1).

on the binary phases before and after having worked at 450 °C for 14 h. Table 5 compares the intrinsic conversion of isobutene and intrinsic yield to methacrolein on the same samples.

At 420 °C, despite the fluctuation of the performances likely originating from the difficulty to measure low conversions, Sb_2MoO_6 presented an overall slight increase of the conversion with the time of reaction with a simultaneous clearly marked increase of the selectivity to methacrolein. $Sb_mMo_{10}O_{31}$ exhibited a more pronounced increase of conversion than Sb_2MoO_6 with a slight increase of the selectivity to methacrolein.

At 450 °C, the conversion of isobutene measured for Sb₂MoO₆ increased continuously throughout the 14 h of reaction (Figure 5). The selectivity to methacrolein remained constant at 32%. When comparing the performances at 420 °C, it turned out that the selectivity to methacrolein (Table 4) and the intrinsic conversion (Table 5) were enhanced after that Sb₂MoO₆ was reacted at 450 °C. Sb_mMo₁₀O₃₁ presented a constant conversion at 450 °C both during the 14 h experiment (Figure 5) and the 8 days experiment. For both tests, the selectivity to methacrolein stabilized at 23.7%. Comparing the performances of this oxide before and after the reaction at 450 °C, an important decrease of the intrinsic conversion was observed (Table 5), but the selectivity to methacrolein increased significantly (Table 4).

3.1.3. Synergetic Effects between Sb-Mo-O Phases and Simple Oxides. Table 6 presents the catalytic performances measured at 420 °C for the mechanical mixtures of Sb-Mo-Ophases with simple oxides (MoO₃ or α -Sb₂O₄). The performances obtained with the pure phases used alone in the reaction are also shown. The values in parentheses correspond to the TABLE 7: Observed and Theoretical Intrinsic Conversion of Isobutene, Intrinsic Yield, and "Intrinsic" Selectivity (Calculated by Reporting Intrinsic Yield to Intrinsic Conversion) to Methacrolein on the Mixtures of Sb-Mo-O Phases with Simple Oxides at 420 °C^a

catalyst	%C m ⁻²	$% Y(meth) \atop{m^{-2}}$	%S(meth) "intr."
Sb ₂ MoO ₆ Sb _m Mo ₁₀ O ₃₁ MoO ₃ α-Sb ₂ O ₄	24.4 54.1 21.9 9.4	3.0 8 1.5 0.0	12.5 14.7 6.7 0.0
$\begin{array}{l} Sb_2MoO_6 + MoO_3 \ 50/50 \ (wt \ \%) \\ Sb_2MoO_6 + \alpha - Sb_2O_4 \ 50/50 \ (wt \ \%) \\ Sb_mMo_{10}O_{31} + MoO_3 \ 50/50 \ (wt \ \%) \\ Sb_mMo_{10}O_{31} + \alpha - Sb_2O_4 \ 50/50 \ (wt \ \%) \end{array}$	24.7 (23.1) 18.4 (16.9) 25.6 (38.0) 26.9 (31.8)	5.4 (2.3) 4.2 (1.5) 3.6 (4.7) 3.9 (4.0)	22.1 (9.7) 22.7 (9.0) 14.2 (12.4) 14.7 (12.6)
$MoO_3 + \alpha - Sb_2O_4 \ 50/50 \ (wt \ \%)$	26.5 (15.7)	12.4 (0.7)	46.7 (4.7)

^{*a*} The theoretical values (in parentheses) were calculated assuming the absence of cooperation on the basis of the mass-ponderated conversions and yields to methacrolein of the pure phases tested alone (see eq 1).

theoretical values that should have been measured if the phases in the mixtures had behaved independently without any cooperation. Table 7 displays the same information considering the intrinsic performances of the catalysts. As a reference, the activity of a mixture of MoO₃ and α -Sb₂O₄ 50/50 (wt %) is mentioned. Both Tables 6 and 7 display the arithmetically averaged performances of the complete 3 h test.

Cooperation effects were detected when Sb_2MoO_6 was mixed both with MoO_3 and with α -Sb₂O₄. Only small enhancements of the intrinsic conversion of isobutene were observed for the mixtures (Table 7), but important improvements of the selectivity to methacrolein were obtained (Table 6). The synergetic effect was slightly higher when Sb_2MoO_6 was mixed with α -Sb₂O₄ than with MoO₃.

Both mixtures of Sb_mMo₁₀O₃₁ with MoO₃ and with α -Sb₂O₄ exhibited only synergetic improvement of the selectivity to methacrolein (Table 6). The cooperation was more pronounced when using α -Sb₂O₄ in the mixture than when using MoO₃. The magnitude of the cooperative effects with Sb_mMo₁₀O₃₁ nevertheless remained weaker than that observed with Sb₂MoO₆ and MoO₃ or α -Sb₂O₄.

The most pronounced synergy observed in this series of catalytic tests, considering both intrinsic activity and selectivity to methacrolein, was measured for the mixture of MoO_3 with α -Sb₂O₄.

3.2. Characterization. 3.2.1. Conventional X-ray Diffraction. When comparing the XRD pattern obtained for the fresh Sb_2MoO_6 and those obtained after 3 h of catalytic test at 420 °C and after 14 h at 450 °C, the intensities of the reflection lines did not present significant differences. But five small peaks that could not be assigned to Sb_2MoO_6 appeared on the patterns obtained after tests with intensities increasing with reaction time. These peaks appeared at 21.8, 23.8, 30.3, 33.7, and 47.7°.

Attempts to assign the five new peaks to combinations of another Sb–Mo–O phase with an antimony oxide were unsuccessful. But the assignment of all the peaks was possible using a combination of α -Sb₂O₄ (JCPDS file 11-0694) with Mo₉O₂₆ (JCPDS file 05-0441). Combinations of other simple oxides were not fitting so closely. The conclusion is that a part of Sb and Mo from Sb₂MoO₆ segregates and recrystallizes during the catalytic reaction to α -Sb₂O₄ and Mo₉O₂₆.²¹ Figure 6 shows the evolution of the XRD patterns of Sb₂MoO₆ with the time of catalytic reaction.



Figure 6. XRD patterns of (a) fresh Sb₂MoO₆, (b) Sb₂MoO₆ after 3 h of catalytic test at 420 °C and (c) after 14 h of catalytic test at 450 °C. The arrows pointing up indicate the five peaks appearing after catalytic tests: * for Mo₉O₂₆, \bigcirc for α -Sb₂O₄.

Considering the other Sb–Mo–O oxides, all the peaks corresponding to Sb₄Mo₁₀O₃₁ got progressively extinct with increasing time of reaction. These were the peaks at 13.9, 18.4, 26.0, 28.1, 36.1, 36.9, 42.8, 49.7, 53.4, and 53.9°. The peaks corresponding to Sb₂Mo₁₀O₃₁ remained unchanged in position, but the sample exhibited a tendency to amorphization. Two new peaks appeared at 51.5 and 54.2°. These corresponding to another Sb–Mo–O phase or to an MoO_{3-x} phase was detected. The conclusion is that Sb₄Mo₁₀O₃₁ recrystallizes to α -Sb₂O₄ and very likely to Sb₂Mo₁₀O₃₁, which seems to be relatively stable. Figure 7 shows the evolution of the duration of the catalytic test.

3.2.2. In situ X-ray Diffraction. When Sb₂MoO₆ was maintained in air at 420 °C, all the reflection lines corresponding to this phase progressively vanished. They were completely extinct after the measurement of three patterns (about 6 h). In the same way, four new peaks progressively appeared at 25.6, 27.2, 28.8, and 33.7°, showing that MoO₃ and α -Sb₂O₄ crystallized during the experiment. The same phase segregation was observed when the experiments were conducted at increasing temperatures. The patterns measured at low temperatures (200 and 300 °C) did not differ from that of the fresh Sb₂MoO₆, but those measured at 500 and 600 °C only presented the peaks typical of MoO₃ and α -Sb₂O₄. At 400 °C, the pattern was composed of a combination of Sb₂MoO₆, MoO₃, and α -Sb₂O₄. Figure 8 shows the evolution with time of the XRD pattern of Sb₂MoO₆ maintained at 420 °C.

Similar results were obtained with Sb_mMo₁₀O₃₁. When the sample was maintained at 420 °C, the lines corresponding to Sb₄Mo₁₀O₃₁, mainly 25.8, 28.0, 35.9, and 36.8° completely vanished after the first scan (about 2 h). Simultaneously, reflections assigned to MoO₃, with some α -Sb₂O₄ lines, appeared. The lines of Sb₂Mo₁₀O₃₁ remained unchanged after the completion of the whole analysis cycle.

When looking at the evolution of the patterns with the temperature, the decomposition of $Sb_4Mo_{10}O_{31}$ to a mixture of



Figure 7. XRD patterns of (a) fresh Sb_mMo₁₀O₃₁, (b) Sb_mMo₁₀O₃₁ after 3 h of catalytic test at 420 °C, (c) after 14 h, and (d) after 8 days of catalytic test at 450 °C. The arrows # pointing down indicate the disappearing peaks of Sb₄Mo₁₀O₃₁, the arrows \bigcirc pointing up indicate the appearing peaks of α -Sb₂O₄.



Figure 8. Evolution with time of the XRD pattern of Sb_2MoO_6 maintained at 420 °C. The arrows pointing up indicate the new peaks appearing during the analysis: * for MoO_3 , \bigcirc for α -Sb₂O₄. + indicates the peaks corresponding to the Pt sample holder.

MoO₃ with α -Sb₂O₄ was detected at 400 °C. When reaching 500 °C, the lines corresponding to Sb₂Mo₁₀O₃₁ also started to vanish. They got completely extinct at 600 °C. This concerned the lines at 21.8, 24.3, 26.1, 26.5, 30.4, 34.3, 34.6, 43.8, 44.6, and 48.5°. No other lines than those of MoO₃ and α -Sb₂O₄ were detected. Figure 9 shows the evolution of the XRD patterns of Sb_mMo₁₀O₃₁ with the temperature of analysis.

The conclusion of this section is that, in air, both Sb–Mo–O phases tend to decompose to a mixture of MoO₃ and α -Sb₂O₄.



Figure 9. Evolution with temperature of the XRD patterns of $Sb_mMo_{10}O_{31}$. Arrows pointing down indicate the disappearing peaks, respectively, \wedge for $Sb_2Mo_{10}O_{31}$ and # for $Sb_4Mo_{10}O_{31}$; arrows pointing up indicate the appearing peaks of $MoO_3 *$ and α -Sb₂O₄ \bigcirc ; + indicates point the peaks of the Pt sample holder.

The decomposition starts between 300 and 400 $^{\circ}$ C for Sb₂MoO₆ and Sb₄Mo₁₀O₃₁, and between 400 and 500 $^{\circ}$ C for Sb₂Mo₁₀O₃₁.

3.2.3. Confocal Laser Raman Microscopy (LRS). Confocal Raman mapping of a $30 \times 40 \,\mu\text{m}^2$ area of fresh Sb₂MoO₆ gave identical spectra. This confirmed the XRD observation (section 2.1.1.1) that the fresh Sb₂MoO₆ sample was homogeneous and contained only one crystalline phase. One representative LRS spectrum of the fresh Sb₂MoO₆ is given in Figure 10a. Bands were measured at 126, 137w, 151s, 157sh, 168s, 180, 205sh, 213s, 221sh, 248, 276vs, 289s, 310sh, 317, 337w, 369vw, 383sh, 393s, 435w, 477, 543vw, 594w, 713s, 746, 813vvs, 845sh, and 937 cm⁻¹.

After 14 h of catalytic reaction at 450 °C, the surface of Sb₂MoO₆ appeared less homogeneous than the fresh material. Two equally well represented types of spectra were detected by confocal Raman mapping of the reacted sample. The first type of spectrum (Figure 10b, spectrum A) exhibited the pattern found for the fresh material. Even if presenting all the strongest bands measured for the fresh sample, these spectra were generally less intense and had a lower signal-to-noise ratio than those from fresh Sb₂MoO₆. Thus, the weak bands at 137w, 157sh, 205sh, 310sh, 369vw, 383sh, 435w, and 543vw could not be resolved from the noise. The other type of Raman spectrum (Figure 10b, spectrum B) had low intensity and low signal-to-noise ratio. Only the most intense peaks of the fresh material were observed as broad bands at 210, 273, 389, 716, and 812 $\rm cm^{-1}.~$ In addition to these, some bands that were not observed for the fresh Sb₂MoO₆ were measured at 191, 234, 263, 457, 495sh, 660, and 880 cm⁻¹. According to the assignment given by Mestl et al., these new bands indicated the presence of slightly reduced α -Sb₂O₄ (bands at 191, 263, and 457 cm⁻¹) and MoO_{3-x} (bands at 234, 495, 660, and 880 cm^{-1}) species at the surface of the sample.²²⁻²⁴ Figure 10b shows the two types of Raman spectra recorded for the reacted Sb₂MoO₆. Our conclusion is that Sb₂MoO₆ decomposes during catalysis at least partially to a mixture of MoO_{3-x} and α -Sb₂O₄.



Figure 10. LRS spectra representative of the Sb₂MoO₆ fresh (a) and after catalytic reaction at 450 °C over 14 h (b, the "S's" indicate the position of the bands assigned to α -Sb₂O₄ and the "M's" those of the bands assigned to MoO₃).

Three types of Raman spectra were recorded for the fresh $Sb_mMo_{10}O_{31}$ sample according to the 750 spots analyzed. The first type of spectrum (Figure 11a, spectrum A) represented about 90% of the area measured in confocal Raman mapping and was therefore assigned to the $Sb_2Mo_{10}O_{31}$ fraction of the sample. These spectra presented bands at 132vw, 140w, 170vw,



Figure 11. LRS spectra representative of the $Sb_mMo_{10}O_{31}$ fresh (a) and after catalytic reaction at 450 °C over 14 h (b).

183vw, 192, 213, 225, 238, 253vw, 268s, 286, 302, 308sh, 331, 352, 376sh, 393s, 437sh, 466vs, 505w, 551vw, 658w, 697w, 714sh, 782, 816s, 878w, and 884 cm⁻¹. About 5% of the area analyzed exhibited the LRS pattern with all the bands observed for Sb₂MoO₆ (Figure 11a, spectrum B). The third type of Raman spectrum (Figure 11a, spectrum C) represented about 5% of the measured area on Sb_mMo₁₀O₃₁. It exhibited very weak bands at 202, 227, 347, 362, 457, 466, 495, 568, 589,

TABLE 8: Specific Area Measurements SBET for the Sb–Mo–O Phases before and after Catalytic Reaction at 450 $^\circ \rm C$ for 14 h

catalyst	SBET before reaction $(m^{2 g-1})$	$\frac{\text{SBET after reaction}}{(m^{2g-1)}}$
$\frac{Sb_2MoO_6}{Sb_mMo_{10}O_{31}}$	0.38 0.17	0.27 0.35

and 741 cm⁻¹. This perfectly fits with the pattern assigned to MoO_2 by Spevack and McIntyre.²⁵ Sb₂MoO₆ and MoO₂ were not detected in Sb_mMo₁₀O₃₁ by XRD. However, we can reasonably assume that traces of Sb₂MoO₆ might remain in Sb_mMo₁₀O₃₁. As already proposed in section 2.1.1.2 for the presence of crystalline MoO_{3-x} phases, the presence of MoO₂ could originate from the formation of binary phases, like Sb₄Mo₁₀O₃₁ and Sb₂MoO₆, containing more Sb than Sb₂Mo₁₀O₃₁, with consequently the simultaneous formation of molybdenum oxide species.

After the catalytic reaction, the Raman mapping of the reacted Sb_mMo₁₀O₃₁ did not show any Raman spectra presenting the typical features of Sb₂MoO₆ or of MoO₂. Raman spectra exhibiting the bands assigned to Sb₂Mo₁₀O₃₁ were still observed. However, this only concerned about 50% of the area measured. The Sb₂Mo₁₀O₃₁ spectra exhibited a lower signal-to-noise ratio than the unreacted material with the consequence that the weakest bands of the spectrum were not or less resolved (Figure 11b, spectrum A). In addition, about 50% of the measured area exhibited a Raman pattern that was not observed for the fresh Sb_mMo₁₀O₃₁ sample. This presented bands at 112w, 125w, 153s, 195, 214w, 240, 280s, 287sh, 334, 362sh, 376, 466w, 504vw, 665, 817vs, 878w, and 995s cm^{-1} with high intensities and a high signal-to-noise ratio (Figure 11b, spectrum B). These features, in particular the strong band at 995 cm⁻¹ (Mo=O stretch involving Mo atoms in an octahedral coordination), are very typical of MoO₃. However, the presence of a small signal at 878 cm⁻¹ (Mo=O stretch involving Mo atoms in a more tetrahedral coordination) indicated the possibility that a fraction of the MoO₃ formed after reaction was very slightly reduced to a MoO_{3-x} species.²² As the Raman spectra exhibiting the bands of MoO_{3-x} represent 50% of the area measured on the reacted sample, it is precluded that this originates exclusively from the reoxidation of the MoO₂ and from the decomposition of the Sb₂MoO₆ fractions of the fresh material: as each of these phases represented only 5% of the area measured on the fresh sample, then if MoO_{3-x} only originated from the decomposition of Sb₂MoO₆ and the reoxidation of MoO₂, one would thus obtain only 10%, at the maximum, of the area measured on the reacted sample with a Raman spectrum typical of MoO_{3-x} . Even if we did not detect any Raman spectrum with the features typical of a simple Sb oxide (likely because being formed in 10 times smaller amount than MoO_{3-x}), the conclusion is thus that the formation of simple Mo and Sb oxides mainly results from the decomposition during catalysis of Sb_mMo₁₀O₃₁ to simple oxides.

3.2.4. Specific Area Measurement. Table 8 shows the SBET values measured for the pure Sb–Mo–O phases before and after the catalytic activity measurement performed at 450 °C over 14 h. Sb₂MoO₆ presented a lower SBET value after the test than before, but for Sb_mMo₁₀O₃₁ the SBET value measured after the test was higher than before.

3.2.5. Scanning Electron Microscopy. Figure 12 shows SEM views of the fresh Sb₂MoO₆ sample and of the sample after the catalytic test at 450 °C. Before being catalytically tested (Figure 12a), pure Sb₂MoO₆ was composed of small crystallites with sizes varying between 500 nm and 10 μ m and without any well-defined morphology. After 14 h of test at 450 °C (Figure 12b),



Figure 12. Scanning electron microscopy views of Sb₂MoO₆ (a) fresh (length of the bar = 15 μ m) and (b) after catalytic test at 450 °C for 14 h (length of the bar = 30 μ m).

the sample was mainly composed of large compact aggregates of small crystallites. The aggregates, with sizes between 15 and 30 μ m, exhibited an imperfect prismatic morphology.

Fresh Sb_mMo₁₀O₃₁ was mostly composed of large crystals of 20–40 μ m exhibiting an octagonal prismatic morphology. The thickness of the prisms varied in a large extent. The crystallographic faces were flat and smooth. With increasing time and temperature of the catalytic activity measurement, a recrystallization progressively took place on the crystals. For the sample tested 3 h at 420 °C, most of the crystals presented fragmented faces. Newly formed small crystallites with illdefined morphologies were already distinguishable on some big crystals. After 14 h at 450 °C, the crystals having undergone the recrystallization were more numerous. The morphology of the new crystallites was more defined and corresponded to thin platelets. After 8 days of catalytic test, the recrystallization had further progressed as all the starting crystals had recrystallized and as the size of the new crystallites had increased. A sequence of four pictures showing the progress of the recrystallization is shown in Figure 13.

4. Discussion

4.1. Possible Role of the Sb–Mo–O Phases. 4.1.1. Selectivity to Methacrolein of the Pure Binary Sb–Mo–O

Phases. Our objective was to explore the role that binary phases associating Sb, Mo, and O could play in the synergetic effects observed with mechanical mixtures of MoO₃ and α -Sb₂O₄. The first point to investigate was whether such Sb-Mo-O phases could possess very high catalytic performances, and hence whether their possible formation during the test could explain the enhancement of selectivity to methacrolein detected for the oxidation of isobutene on mixtures of simple oxides. On one hand, Sb₂MoO₆ appeared intrinsically less active than the mixture of MoO₃ with α -Sb₂O₄ with the similar atomic composition, but Sb_mMo₁₀O₃₁ was intrinsically more active than the corresponding mixture. On the other hand, at comparable low conversions of isobutene, the selectivities to methacrolein of both Sb-Mo-O phases considered in this work were always lower than those of the mixtures of MoO₃ with α -Sb₂O₄ with similar atomic compositions: 0.0% with Sb₂MoO₆ but 45.4% with the corresponding mixture and 13.7% with $Sb_mMo_{10}O_{31}$ but 25.2% with the corresponding mixture. An even bigger gap appears when comparing the selectivities of the Sb-Mo-O phases with that of the mechanical mixture containing the oriented (010)-MoO₃ and α -Sb₂O₄ where the formation of Sb₂Mo₁₀O₃₁ was suspected to happen *in operandi*. This mixture exhibited a 36.7% selectivity to methacrolein obtained at a much higher conversion of isobutene (57.1%).¹ Hence, our conclusion is that the presence of Sb-Mo-O phases, in case they would form in operandi starting from the simple oxides mixtures, could not explain the high selectivities to methacrolein measured for these mixtures.

4.1.2. Cooperation between Binary Sb-Mo-O Phases and Simple Oxides. Another possible role of the Sb-Mo-O phases in the synergism existing between MoO_3 and α -Sb₂O₄ is the existence of a cooperation between one of the binary phases and one of the simple oxides. Qualitatively, the results indicate that such effects might exist. For all the mixtures containing a binary phase and a simple oxide, catalytic synergisms were found when considering the selectivity to methacrolein. In addition, synergetic effects were also observed for the intrinsic conversion of isobutene on the mixtures containing Sb₂MoO₆ and MoO₃ or α -Sb₂O₄. But the synergisms detected with these mixtures were always weaker than those measured when mixing the simple oxides directly. It is therefore unlikely that the synergism between the simple oxides is exclusively, or even significantly, due to the formation of Sb-Mo-O phases during the catalytic reaction. Nevertheless, one cannot completely discard this hypothesis without further arguments, mainly because very few attempts to improve the synthesis procedure of the Sb-Mo-O phases and to increase their specific areas had been made in order to maximize the cooperations (as it was done previously for the mixtures of MoO₃ with α -Sb₂O₄). Therefore, further discussion of these results cannot be dissociated from the observation, on one hand, of the evolution with time on stream of the catalytic performances of the Sb-Mo-O phase and, on the other hand, of their progressive recrystallization under the conditions of reaction or under conditions close to the conditions of reaction.

4.1.3. Evolution of the Performances and of the Morphology of the Binary Sb-Mo-O Phases with Time on Stream. In all the catalytic tests shown in this work, the performances of the pure Sb-Mo-O phases improved with the time of reaction. For both Sb-Mo-O phases, an increase of the conversion of isobutene took place with the time on stream. In the case of $Sb_mMo_{10}O_{31}$, this improvement of the conversion is very likely related to its tendency to have its specific area increasing during the catalytic reaction (Table 8). But the increase of conversion



Figure 13. Scanning electron microscopy view of the progressive recrystallization of $\text{Sb}_m\text{Mo}_{10}\text{O}_{31}$ with the duration of catalytic reaction: (a) fresh (length of the bar = 30 μ m), (b) after 3 h of test at 420 °C (length of the bar = 5 μ m), (c) after 14 h of test at 450 °C (length of the bar = 6 μ m), and (d) after 8 days of test at 450 °C (length of the bar = 500 nm).

observed for Sb₂MoO₆ cannot be due to such an effect because the specific area was shown to decrease during the reaction. These conclusions are confirmed when comparing the intrinsic activities at 420 °C before and after the catalysts were maintained at 450 °C for a long time. In the case of Sb₂MoO₆, an important increase of the intrinsic conversion was measured. But for $Sb_mMo_{10}O_{31}$, an important decrease of the intrinsic conversion of isobutene was obtained after the reaction at 450 °C (Table 5). The evolution of the selectivity to methacrolein with time on stream and the comparison of the selectivities obtained at 420 °C before and after the reaction at 450 °C are easier to interpret because these were always measured at comparable low conversion and were not influenced by the variation of the specific area of the catalysts. For both binary phases, an increase of the selectivity to methacrolein with time on stream was observed. Also, these were higher after that the catalysts were maintained at 450 °C for 14 h. In both cases, these results show that, under the conditions of reaction, the Sb-Mo-O phases progressively transformed to new structures exhibiting other catalytic performances. In the case of Sb₂MoO₆, the new structure was intrinsically more active and more selective than the fresh binary phase; in the case of $Sb_mMo_{10}O_{31}$,

the new structure was intrinsically less active but was more selective to methacrolein than the fresh material.

These behaviors have to be further interpreted in view of the other changes of characteristics that the catalysts undergo. LRS and XRD analyses of the catalysts before and after catalytic tests as well as the *in situ* XRD measurements (in the presence of air in the high-temperature XRD cell) showed that the Sb-Mo-O compounds were unstable under the conditions of reactions. The part of the discussion that follows is intended to confirm that the above effects are due to the decomposition of the Sb-Mo-O phases to simple oxides.

The LRS analyses indicated that Sb₂MoO₆ dissociated to some extent to a mixture of MoO_{3-x} and α -Sb₂O₄. The XRD analyses revealed an identical behavior for the bulk of Sb₂MoO₆ that decomposed, at least partially, to α -Sb₂O₄ and Mo₉O₂₆ crystallites. Similarly, in the *in situ* XRD analyses, Sb₂MoO₆ decomposed completely to a mixture of α -Sb₂O₄ and MoO₃. The phenomenon started between 300 and 400 °C, namely, below the temperature of the catalytic tests. Sb₂MoO₆ transformed to different simple oxides in the experiments that compare the samples before and after catalysis and in the *in situ* XRD measurements. This was most likely the consequence of the different amount of oxygen available for the Sb–Mo–O to undergo the oxidation associated with the decomposition. When a sufficient amount of oxygen was supplied like in the *in situ* experiments, MoO₃ was formed. In the catalytic reaction, the concentration of oxygen in the reaction gas was the same as in air, but part of it was used for the oxidation of isobutene. The amount of oxygen available for the reoxidation of the binary phase being lower, a molybdenum suboxide was formed because Mo could not fully reoxidize. Both sets of results thus reflect the instability of Sb₂MoO₆ in the presence of oxygen and its tendency to decompose to a mixture of simple oxides.

Similar differences between ex situ and in situ XRD experiments were noted for $Sb_m Mo_{10}O_{31}$. In the conditions of reaction, $Sb_4Mo_{10}O_{31}$ transformed to α - Sb_2O_4 and $Sb_2Mo_{10}O_{31}$. The latter only underwent a slight amorphization. In the in situ analyses, both phases decomposed to α -Sb₂O₄ and MoO₃. The transition occurred between 300 and 400 °C for Sb₄Mo₁₀O₃₁, and between 400 and 500 °C for Sb₂Mo₁₀O₃₁. Although our XRD results do not give a direct proof, the detection of a strong MoO_{3-r} signal in the LRS measurement of the used Sb_mMo₁₀O₃₁ constitutes an undisputable argument to conclude that even in the conditions of reaction Sb₂Mo₁₀O₃₁ particles decomposed during catalysis to simple oxides. This behavior might explain the amorphization detected by XRD for the reacted sample. The simple oxide crystallites formed were certainly very small with likely weak crystallinity and were only present in small amount. This might explain why the conventional ex situ XRD analyses did not unequivocally detect new reflection lines corresponding to simple oxides. The sequence of four SEM pictures showing the progressive recrystallization of $Sb_mMo_{10}O_{31}$ was difficult to interpret and did not allow one to determine the nature of the small crystallites formed at the surface of the $Sb_mMo_{10}O_{31}$ crystals. Their platelet morphology does not correspond to that classically found for α -Sb₂O₄ crystals. But, it exactly corresponds to that of MoO₃ crystals. Moreover, SEM pictures obtained after 8 days of reaction showed that the surface of all crystals was modified. This precluded the possibility that only the crystals of the $Sb_4Mo_{10}O_{31}$ phase had transformed with, in this case, the newly formed crystallites observed corresponding to $Sb_2Mo_{10}O_{31}$. This additional result shows that $Sb_2Mo_{10}O_{31}$ was also undergoing the recrystallization to simple oxides. Our conclusion is thus that $Sb_mMo_{10}O_{31}$ is unstable in the conditions of reaction and that both Sb₂Mo₁₀O₃₁ and Sb₄Mo₁₀O₃₁ tend to decompose and to recrystallize at the surface to an MoO_{3-x} phase and α -Sb₂O₄.²⁶

Our observations of the decomposition of the Sb-Mo-O phases under the conditions of reaction go in parallel with the conclusions reported by Parmentier et al., namely, that the binary phases were unstable in the presence of oxygen.¹⁶⁻¹⁹ Differences only appeared when comparing the temperatures at which the phases were observed to recrystallize. Parmentier et al. reported the decomposition to simple oxides at 400 °C for Sb₂MoO₆, at 300 °C for Sb₄Mo₁₀O₃₁, and at 350 °C for $Sb_2Mo_{10}O_{31}$. We do not have any explanation for these differences. Parmentier had only reported the transition of the Sb-Mo-O phases in air. No attempt to evaluate the occurrence of the phenomenon in slightly oxygen-deficient conditions such as in catalytic oxidation reactions had been done. The work of Parmentier was not sufficient to totally prove the instability of the Sb-Mo-O phases or to predict the occurrence of their decomposition to simple oxides under the catalytic conditions. The present investigation leads us to conclude that this decomposition actually takes place.

There is therefore an unambiguous connection between (i) the aforementioned improvement with the time on stream of the performances of the Sb-Mo-O phases and (ii) the partial decomposition of these phases to mixtures of simple MoO_{3-x} and α -Sb₂O₄. The formation of MoO_{3-x} and α -Sb₂O₄ crystals at the surface of $Sb_mMo_{10}O_{31}$ and Sb_2MoO_6 samples is the phenomenon responsible for the increases of conversion of isobutene and of selectivity to methacrolein. The decomposition of the binary phases also fully explains the difference observed when comparing the performances of the catalysts before and after having been reacted at high temperature for a long time (Tables 4 and 5). Sb₂MoO₆ is initially intrinsically less active and less selective than the mixture of MoO₃ with α -Sb₂O₄ with the same atomic composition (Tables 2 and 3). Hence, after it has decomposed to simple oxides after a long duration test, it is logical that the performances of Sb₂MoO₆ have improved. The initial intrinsic activity of $Sb_mMo_{10}O_{31}$ is higher than that of the corresponding mixture of MoO₃ with α -Sb₂O₄, but its selectivity to methacrolein is lower. Hence, it is logical to observe, after its partial decomposition to simple oxides, a decrease of the intrinsic activity with simultaneous increase of the selectivity of the catalyst. These results further confirm that the synergetic improvement of the selectivity to methacrolein obtained when using mixtures of MoO₃ with α -Sb₂O₄ cannot be explained by the formation of Sb-Mo-O phases.

4.2. Role of the Cooperation between the Simple Oxides Formed at the Surface of the Decomposed Sb–Mo–O Phases. As our results show the formation of α -Sb₂O₄ and of MoO_{3-x}, it is necessary to focus further on the role played by the simple oxide phases formed at the surface of the binary phases on the improvement of their performances with time on stream. We base the following discussion on the cooperation between separate (not mutually contaminated) MoO₃ and α -Sb₂O₄ as already reported elsewhere.³

4.2.1. Influence on the Evolution with Time on Stream of the Performances of the Binary Phases. On this base, it is possible to explain more in detail the extent to which the improvements of the catalytic performances of the Sb-Mo-O samples took place as a function of the time on stream. For Sb₂MoO₆, as shown by the *in situ* XRD analyses, the decomposition to a mixture of MoO_{3-x} and α -Sb₂O₄ occurred relatively easily. During the catalytic test at 420 °C, the isobutene conversion remained low during the first moments of reaction likely because only small amounts of the simple oxides were formed. But, on the other hand, the selectivity to methacrolein reached rapidly its highest value because this already corresponded to that obtained with a mixture of MoO_{3-x} and α -Sb₂O₄ with a high proportion (67 wt %) of α -Sb₂O₄, which is in the range reported to be highly selective.³ For longer times of reaction, the formation of MoO_{3-x} and α -Sb₂O₄ progressed more deeply in the bulk of Sb₂MoO₆ crystals. This was evidenced by the SEM picture and by the appearance of XRD peaks corresponding to the simple oxides. With the number of simple oxides crystallites formed increasing, the conversion of isobutene consequently also continuously increased. The selectivity, however, remained constant because the relative proportion of the simple oxides formed remained dictated by the stoichiometry of the starting antimony molybdate, namely, remained constant, with a high Sb content.

A similar mechanism can be proposed for $Sb_mMo_{10}O_{31}$. The situation is slightly more difficult to interpret because the decomposition temperature was higher than for Sb_2MoO_6 . The fact that the evolution of its performances with time was slower corresponded to the higher stability at higher temperature. One

can reasonably assign the rapid increase of the conversion of isobutene to the surface decomposition of $Sb_mMo_{10}O_{31}$ to simple oxides. For longer times of reaction, the conversion, however, did not increase anymore even at a higher temperature. Our hypothesis is that the recrystallization could not progress deeply in the bulk. This would be due to the fact that the decomposition of $Sb_mMo_{10}O_{31}$ necessitates much oxygen. The decomposition of the bulk was thus impossible (or very slow) because of the likely small flow of oxygen diffusing into the core of the large initial Sb_mMo₁₀O₃₁ crystals (or because of the fact that bulk diffusion in the corresponding structure is very slow). The same weak oxygen concentration in the bulk probably also existed when considering Sb₂MoO₆. However, in this case, its decomposition was not stopped because it only required modest amounts of oxygen. The conclusion that the $Sb_mMo_{10}O_{31}$ crystals only recrystallized in the surface is consistent with the SEM observations and could explain why no simple oxides XRD peaks were detected after the catalytic reaction. Considering the selectivity to methacrolein obtained with $Sb_mMo_{10}O_{31}$, it only improved in the first moments of the reaction for similar reasons as for Sb₂MoO₆. A difference was that the improvement of selectivity is low. This is logical. On one hand, $Sb_mMo_{10}O_{31}$ initially exhibited some selectivity to methacrolein. On the other hand, the mixture of MoO_{3-x} and α -Sb₂O₄ formed contained only a small relative proportion (18 wt %) of α -Sb₂O₄, and it is reported that such a composition present lower selectivities to methacrolein than compositions containing more α -Sb₂O₄.³ This explains the modest improvements of selectivity observed.

4.2.2. Influence on the Apparent Cooperation between Binary Phases and Simple Oxides. In light of the unstability of the Sb-Mo-O phases, of their natural tendency to decompose to MoO_{3-x} and α -Sb₂O₄ in contact with air, and of the existence of cooperation between these two simple oxides, one can also explain the occurrence or the absence of synergetic effects in the mixtures containing Sb-Mo-O phases and a simple oxide. The mixture that exhibited the less intense synergetic behavior was that containing $Sb_mMo_{10}O_{31}$ and MoO_3 . Only a weak synergism was observed for the selectivity to methacrolein (Table 6). When decomposing during the reaction, $Sb_mMo_{10}O_{31}$ formed a mixture of MoO_{3-x} and α -Sb₂O₄ with a very small proportion of α -Sb₂O₄. When taking into account the MoO₃ initially present in the mechanical mixture, the resulting overall proportion of α -Sb₂O₄ is small, even negligible, compared to that of MoO₃ admixed and could thus not bring about a significant cooperative effect. The mixture of $Sb_mMo_{10}O_{31}$ with α -Sb₂O₄ resulted after decomposition in a mixture containing more α -Sb₂O₄. Hence, even if no synergism was observed for the conversion, the synergism for the selectivity to methacrolein was higher than for the mixture of $Sb_mMo_{10}O_{31}$ with MoO_3 . For both mixtures involving Sb₂MoO₆, cooperative effects were detected. The decomposition of Sb₂MoO₆ gave rise to a mixture of MoO_3 and $\alpha\text{-}Sb_2O_4$ with a composition 33/67 wt %. The additional supply of one of the two simple oxides resulted in mixtures with overall compositions still suitable for developing cooperations. It is however interesting to point out that the mixture of Sb₂MoO₆ with α -Sb₂O₄, with a higher overall content of α -Sb₂O₄, exhibited also a more important synergism than the mixture of Sb_2MoO_6 with MoO_3 . The results are fully consistent with the interpretation that the special activity of Sb-Mo-O catalysts was due to a cooperation between the simple oxide phases formed in operandi at their surface, namely, α -Sb₂O₄ and MoO₃ (or a slightly reduced MoO_{3-x} phase), rather than to the real performances of binary phases. Figure 14 summarizes this conclusion.27



Figure 14. Schematic interpretation of the catalytic behavior of the Sb-Mo-O phases in the catalytic selective oxidation of isobutene to methacrolein.

5. Conclusion

The presence of an Sb-Mo-O phase cannot explain the synergetic effects observed in mechanical mixtures of MoO₃ with α -Sb₂O₄, neither by its own activity nor by the occurrence of cooperative phenomena. The selectivities to methacrolein of the phases containing Sb, Mo, and O simultaneously, namely, Sb₂MoO₆ on one hand and Sb₂Mo₁₀O₃₁ and Sb₄Mo₁₀O₃₁ on the other hand, are lower than those of mechanical mixtures composed of MoO_3 and α -Sb₂O₄ with comparable atomic compositions. The binary phases decompose under the conditions of the catalytic tests to a mixture of simple molybdenum and antimony oxides. The consequence of this decomposition is that the catalytic performances, in particular the selectivity to methacrolein, of the Sb-Mo-O catalysts improve with the formation of MoO₃ and α -Sb₂O₄ ongoing. The apparent synergetic effects between the Sb-Mo-O phases and the simple oxides also originate from the decomposition of the former to simple oxides. The catalytic properties must be attributed to a cooperation between MoO₃ and α -Sb₂O₄. Our results are in agreement with the predictions of Weng and Delmon and Bing et al. concerning the in operandi instability of the Sb-Mo-O phases.^{3,9,14,28} There is a substantial difference between the behavior of the Sb-Mo-O phases in the conditions of reaction and in experiments roughly mimicking these. The present work, however, shows that there is a link between the model experiments in the absence of isobutene and results of real catalytic experiments.

More generally, these conclusions support the interpretation of the cooperation between MoO₃ (or slightly reduced MoO_{3-x}) and α -Sb₂O₄ in selective oxidation reactions via a remote control mechanism, as this considers that the synergetic effects have to be understood on the basis of phases remaining completely separate and mutually noncontaminated under the conditions of the catalytic reaction.^{3,27}

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