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Further on the mechanism of the synergy between MoO_3 and α-Sb_2O_4 in the selective oxidation of isobutene to methacrolein: Reconstruction of MoO_3 via spillover oxygen

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Abstract

This paper concerns the synergetic effects between a (010) oriented MoO_3 and α-Sb_2O_4 in the oxidation of isobutene to methacrolein at 420°C. The catalysts were prepared by mechanical mixture of the pure oxides prepared separately. Important increases were observed both for the conversion of isobutene and for the selectivity to methacrolein, suggesting that new selective sites have been created. The characterization of the samples before and after the reaction by SEM and XRD shows an important reconstruction of the (010) face of MoO_3 into steps exposing (100) faces, when the reaction is carried out in the presence of α-Sb_2O_4. It is known from literature that the (100) face of MoO_3 performs selectively partial oxidation, while the (010) face is not selective. On the other hand, α-Sb_2O_4 has shown to produce spillover oxygen, which flows onto the MoO_3 surface. It is, therefore, concluded that the increase of selectivity is intimately connected to the reconstruction under the action of spillover oxygen. Spillover oxygen would favour the "selective coordination" of Mo atoms or groups of atoms, typical of (100), at the expense of the "non-selective one", typical of (010). This result corresponds to the theoretical prediction of the Remote Control theory.

Keywords: Remote control; Spillover oxygen; Molybdenum oxide; Antimony oxide; Isobutene

1. Introduction

Biphasic mechanical mixtures of MoO_3 and α-Sb_2O_4 are well-known for presenting synergetic effects in reactions as different as the oxidation of isobutene to methacrolein, the oxidation of ethanol to acetic acid, or the oxygen assisted dehydration of N-ethyl-formamide to propionitrile, and this, in a very wide range of temperatures, extending to below 200°C, as in the dehydration–dehydrogenation of 2-butanol to butene and methyl-ethyl-ketone. More precisely, when using these phases, prepared separately, for making mechanical mixtures, these exhibit higher conversion of the substrate, yields and selectivities for the desired products, and longer lifetime, than those which would be calculated on the basis of the properly averaged sum of the performances measured for the pure phases [1–6].

In the present communication, we focus on the partial oxidation of isobutene at 420°C, for which the synergetic effects between MoO_3 and

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α-Sb_2O_4 are particularly important. In this case, a 50/50 wt% mechanical mixture of the pure phases presented an enhancement of 25% of the selectivity to methacrolein, to the detriment of the total oxidation products (CO and CO_2) and of the product of radical reactions (acrolein). In this case, extensive ''post-reaction'' characterization of the pure oxides and their mechanical mixtures, as well as of artificially contaminated oxides have shown that a mutual contamination between MoO_3 and α-Sb_2O_4 was excluded as an explanation of the observed synergetic effects. This, and complementary measurements, including migration of ^{18}O, supported the interpretation that these effects were due to a ''Remote Control Mechanism'' (RCM) [7,8]. According to this mechanism, α-Sb_2O_4, the ''spillover oxygen donor'', dissociates O_2 to a highly mobile and active oxygen species, namely ''spillover oxygen'' (O_{so}). This species migrates onto the surface of MoO_3, the ''spillover oxygen acceptor'', where it creates new selective sites, regenerates deactivated (reduced) selective sites, and removes coke precursors from the surface [5,6,9–11].

Nevertheless, data concerning the molecular scale changes of the surface of MoO_3 which are at the origin of the creation of new selective sites were still missing. It is known that the (010) basal face and the (100) lateral face of MoO_3 crystallites exhibit ''structural specificities'', namely different properties (Table 1). In the arrangement of atoms on these surfaces, the exposed molybdenum–oxygen bonds are very different. The (010) face mostly brings about total oxidation reactions, while the (100) face selectively performs partial oxidation reactions [12–18].

As the reaction of spillover oxygen with the surface of MoO_3 brings about a modification of selectivity, it was logical to speculate that this should correspond to a surface reconstruction, namely to the formation of surface structures corresponding to more selective coordinations of molybdenum. This could indeed be achieved by replacing the Mo atoms with oxygen coordinations mainly characteristic of the non-selective (010) face, by Mo atoms (or groups of atoms) with coordinations similar or identical to those which cover the surface of the selective (100) face. The investigation of this possibility is the objective of this work. For that, we studied, in the oxidation of isobutene to methacrolein at 420°C, the synergetic effects between α-Sb_2O_4 and a MoO_3 sample developing preferentially the non selective (010) basal face. Characterization of the samples was achieved before and after the tests by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM).

2. Experiments

2.1. Preparation of the catalysts

2.1.1. (010) oriented molybdenum trioxide

A MoO_3 sample developing preferentially basal (010) faces was prepared by recrystallisation of a commercial molybdenum trioxide under a flow of pure O_2 at 600°C during 12 h. The XRD pattern of the obtained solid corresponded to the molybdite phase (ASTM file). The morphology of the crystallites was determined by SEM and verified by XRD, according to the procedure described by Ozkan et al. [16] (Σ

Table 1
Main ''structural specificities'' exhibited by the (010) basal face and the (100) lateral face of MoO_3 crystallites

(010) basal face	(100) lateral face
High reducibility	Low reducibility
Main oxygen coordination: bridging oxygen Mo–O–Mo	Main oxygen coordination: doubely linked oxygen Mo = O
Selective for total oxidation	Selective for partial oxidation

$I_{h00}/\Sigma\ I_{0k0} = 0.003$, where $\Sigma\ I_{h00}$ and $\Sigma\ I_{0k0}$ are the sum of the intensities of the peaks corresponding respectively to the (h00) and (0k0) series). The specific surface area of the sample was 0.75 m^2/g.

2.1.2. Antimony oxide

A commercial Sb_2O_3 was dispersed in concentrated nitric acid at 50°C during 1 hour. After removal of the acid under vacuum, the resulting solid was carefully washed with distilled water and then dried overnight at 110°C. After calcination at 450°C during 20 h, α-Sb_2O_4 was obtained; the surface area was 3.1 m^2/g. XRD showed that the sample contained only the pure cervantite phase (ASTM file).

2.1.3. Mechanical mixture

900 mg of MoO_3 (0.674 m^2) were mixed with 850 mg of α-Sb_2O_4 (2.635 m^2) in 175 ml of n-pentane and thereafter interdispersed ultrasonically during 10 minutes. No mechanical agitation was realized in order not to break or damage the MoO_3 crystallites. The solvent was removed under vacuum at room temperature before the mixture was dried overnight at 80°C. The good interdispersion of the two phases was checked by SEM. Each pure oxide was submitted to the same procedure before the catalytic test.

Fig. 1 shows SEM micrographs of the pure (010) oriented MoO_3, and of the mechanical mixture of this with α-Sb_2O_4.

2.2. Catalytic activity measurement

Catalytic tests were performed in a fixed bed reactor at 420°C. The composition of the gas mixture was isobutene/O_2/He = 1/2/7 (vol.). The total gas flow was 30 ml/min. The mass of catalysts used was respectively 900 mg for pure MoO_3, 850 mg for pure α-Sb_2O_4 and 1750 mg for the mechanical mixture. In order not to change the orientation of the MoO_3, the catalysts were tested as powders without pressing them into wafers. The volume of the catalytic bed was kept constant for all the tests by diluting the catalysts with small glass spheres (previously checked to be inactive). Unreacted isobutene and the methacrolein produced were analysed at the reactor outlet by on-line chromatography. Catalytic activity was expressed in terms of conversion of isobutene (%C) (namely, number of moles of isobutene reacted per 100 moles of isobutene injected), yield (%Y) (namely, number of moles of methacrolein pro-

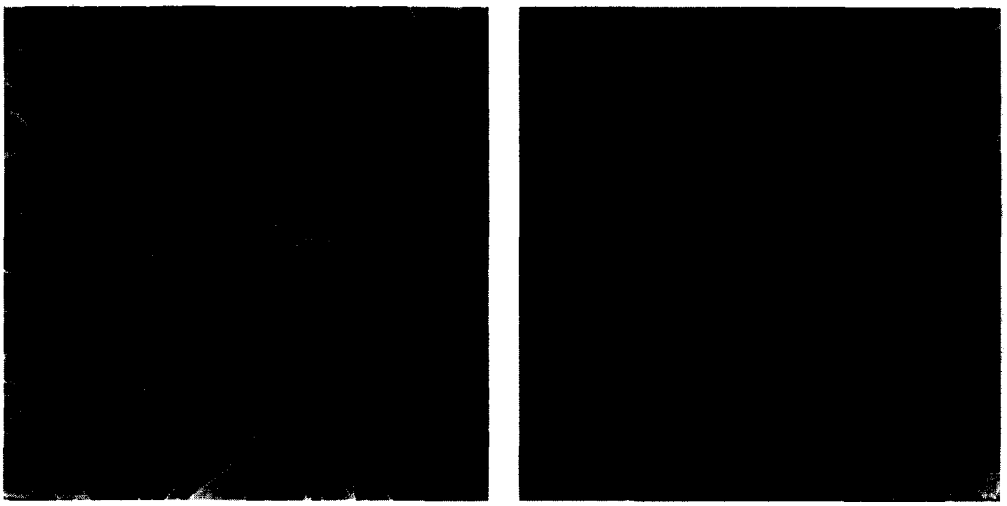


Fig. 1. SEM micrographs of pure (010) oriented MoO_3 having undergone the same preparation procedure as the mixtures (left) and the mechanical mixture of MoO_3 with α-Sb_2O_4 (right).

duced per 100 moles of isobutene introduced) and selectivity to methacrolein (%S) (namely, number of moles of methacrolein produced per 100 moles of isobutene converted). After 3 hours of steady state reaction, the catalysts were cooled down to 25°C at 7.5°C/min in the same flow as during the reaction, and thereafter characterized.

2.3. Characterization

The catalysts were characterized before and after the tests by X-ray diffraction and Scanning Electron Microscopy. XRD was performed in the symmetric analysis mode on a Kristalloflex Siemens D5000 diffractometer using the $K_{\alpha 1,2}$ radiation of Cu ($\lambda = 1{,}5418$ Å) for 2θ angles varying from 10 to 80°. SEM characterization was achieved on a Hitachi S-570 microscope using 15 kV as accelerating voltage. Attention was particularly paid to detecting eventual size, morphology, and orientation modifications, as well as changes on the edges between the different crystallographic faces of MoO_3. All the SEM observations presented in this paper are the results of a careful statistical investigation of the samples carried out by checking the occurrence of the observed features in several different places in the samples.

3. Results

3.1. Catalytic activity measurement

Table 2 summarizes the results of the catalytic tests.

Pure α-Sb_2O_4 and MoO_3 both exhibited low conversions of isobutene, and were totally inactive for the production of methacrolein. On the other hand, the mechanical mixture presented a relatively high conversion with good yield and selectivity to methacrolein. Actually, this result corresponds to the most important synergetic effects ever observed between molybdenum and antimony oxides in the oxidation of isobutene to methacrolein.

Table 2
Observed and theoretical values of the conversion of isobutene (%C), yield (%Y) and selectivity (%S) to methacrolein — Theoretical values (figures in parentheses) are calculated supposing no synergetic effects

Catalyst	Mass tested	%C	%Y	%S
Pure MoO_3	900 mg	3.35	0	0
Mechanical Mixture (900 mg MoO_3 + 850mg Sb_2O_4)	1750 mg	57.09 (10.92)	20.93 (0)	36.67 (0)
Pure α-Sb_2O_4	850 mg	7.57	0	0

3.2. Characterization results

3.2.1. X-ray diffraction

The XRD patterns of the MoO_3 and α-Sb_2O_4 submitted to the mechanical mixture procedure, were identical to those of the fresh pure oxides. The $\Sigma\ I_{h00}/\Sigma\ I_{0k0}$ ratio calculated for MoO_3 was the same as in the pure untreated oxide.

The XRD patterns of the mechanical mixture exhibited all the peaks of the pure oxides, and only these peaks. The intensities corresponded to the composition. Due to the overlapping of some peaks of the molybdenum oxide with some of those of the antimony oxide, it was only possible to obtain a rough estimate of the $\Sigma\ I_{h00}/\Sigma\ I_{0k0}$ ratio of MoO_3. Nevertheless in agreement with the SEM micrographs of the sample (Fig. 1), this showed that the morphology of the MoO_3 crystallites remained unchanged after the mechanical mixture procedure.

The XRD patterns obtained for the pure oxides after test were identical to the ones recorded before the catalytic tests, without any shift or disappearance of peaks, nor appearance of new peaks. The $\Sigma\ I_{h00}/\Sigma\ I_{0k0}$ ratio calculated from the MoO_3 pattern was also unchanged. Fig. 2 shows the XRD patterns obtained for the pure MoO_3 catalysts before and after the reaction.

After the catalytic test, the pattern of the reacted mechanical mixture exhibited all the peaks observed before the test. The $\Sigma\ I_{h00}/\Sigma\ I_{0k0}$ ratio for MoO_3 did not show any significant modification. But two new peaks appeared

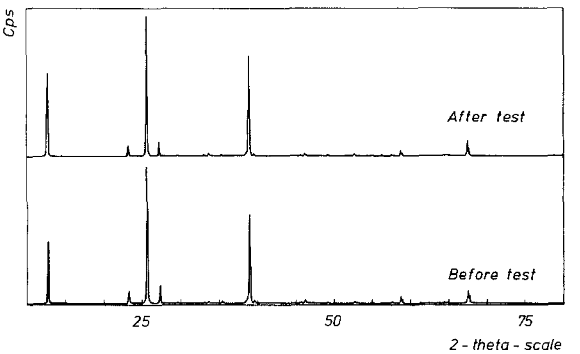


Fig. 2. XRD patterns of pure MoO_3 catalysts before and after the catalytic reaction.

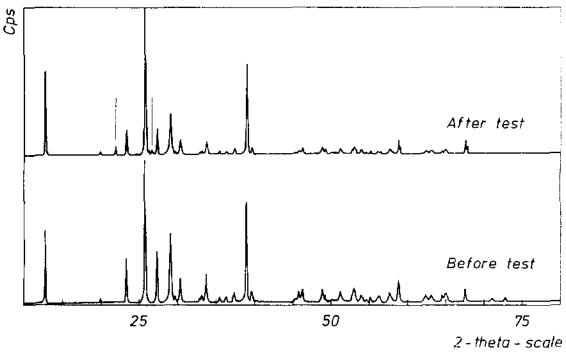


Fig. 3. XRD patterns of the MoO_3 + α-Sb_2O_4 mechanical mixture before and after the catalytic reaction. The lines indicate the positions of the two new peaks appeared after the reaction.

at $2\theta = 22°$ and $2\theta = 26.7°$, respectively representing about 6% and 3% of the intensity of the main peak of the pattern. These peaks could not be attributed to standard patterns of molybdite or cervantite. The peak at 22° fitted perfectly with the standard patterns of Mo_8O_{23} and $Sb_2Mo_{10}O_{31}$ phases. On the other hand the peak at 26.7° only fitted approximately with these standards, especially with the one of $Sb_2Mo_{10}O_{31}$. The other main peaks of these two compounds were not recorded on the spectrum of the mechanical mixture after the test. No other simple or mixed oxide phases patterns, fitting with these two peaks, were found in the ASTM file. Fig. 3 shows the XRD patterns obtained for the mechanical mixture before and after the catalytic test.

3.2.2. *Scanning electron microscopy*

Comparison of the SEM micrographs of the pure MoO_3 and α-Sb_2O_4 before and after the catalytic tests did not reveal any modification of the samples during the reaction, up to a 30.000 × magnification. Fig. 4 shows SEM micrographs of the edge of a MoO_3 crystallite before and after the catalytic reaction in the absence of α-Sb_2O4.

The situation was different for the mechanical mixture. SEM showed important modifica-

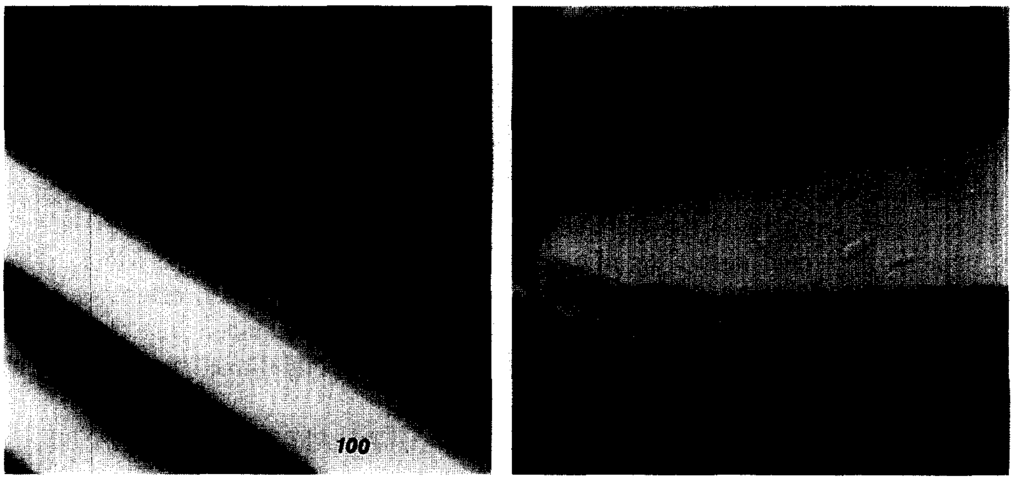


Fig. 4. SEM micrographs of the edge of a MoO_3 crystallite before (left) and after (right) the catalytic reaction in the absence of α-Sb_2O_4.

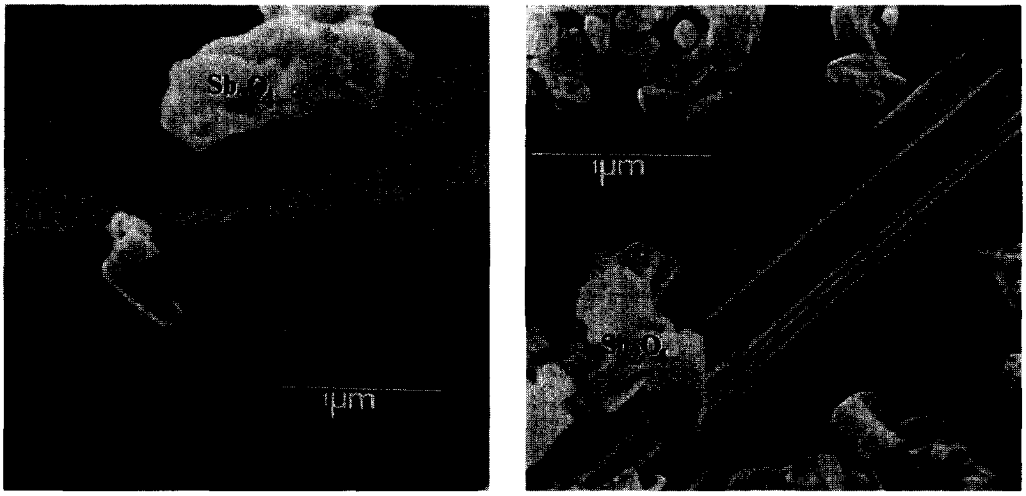


Fig. 5. SEM micrographs of the edge of a MoO_3 crystallite before (left) and after (right) the catalytic reaction in the presence of α-Sb_2O_4. Black arrows indicate the steps formed by the reconstruction of the (010) face to (100) steps.

tions occurring on the molybdenum oxide crystallites after the catalytic test in the presence of α-Sb_2O_4. The edges between the (010) basal face and the (100) lateral faces, which were exhibiting a sharp intersection in the fresh sample, acquired a facetted structure, by developing (100) steps on the (010) faces. This phenomenon was not observed on the MoO_3 tested in the absence of α-Sb_2O_4. Fig. 5 shows SEM micrographs of the edge of a MoO_3 crystallite before and after the catalytic reaction in the presence of α-Sb2O4.

4. Discussion

Activities of both pure MoO_3 and α-Sb_2O_4 were different from those obtained in former investigations of similar catalysts in the same reaction. Indeed antimony oxide was previously reported to be totally inactive in the isobutene oxidation, while it presented here a significant conversion of the substrate in total oxidation products [4]. This is due to the much higher specific surface area of the present α-Sb_2O_4 sample (3.1 m^2/g) when compared with the ones used previously (only 0.4 m^2/g).

The very low selectivity to methacrolein of the present MoO_3 sample has to be compared to that of the samples used in previous experiments which exhibited a selectivity of about 25% to the partially oxygenated product in the same experimental conditions. This is in total agreement with the structural specificities of molybdenum oxide [4]. The present sample is strongly developing the (010) basal face, well known for performing preferentially total oxidation processes, while previous MoO_3 were presenting a more isotropic morphology with higher proportions of the (100) lateral face, selective for partial oxidation reactions.

Considering the mechanical mixture, very strong synergetic effects have been observed between the (010) oriented MoO_3 and α-Sb_2O_4 concerning both the conversion of isobutene, the yield and the selectivity to methacrolein. This observation, and the fact that pure molybdenum oxide was very weakly active and totally unselective, suggest that, in the mechanical mixture, new selective active sites have been created on the surface of the MoO_3. As this phenomenon has not been observed with the pure MoO_3, it is concluded that the creation of the sites is directly linked to the presence of α-Sb_2O_4.

A first hypothesis to explain this phenomenon could be to attribute the changes of catalytic properties to the *in operandi* formation of a new active and selective phase in the catalytic system.

It could indeed be argued that a mixed Sb–Mo–O phase be responsible for the catalytic properties of the mechanical mixture MoO_3 + α-Sb_2O_4. As $Sb_2Mo_{10}O_{31}$ could correspond to some features present on the XRD patterns of the mechanical mixture after the test, one could try to explain the synergetic effect by the presence of this phase. Nevertheless, this hypothesis can be discarded. It has been shown in previous publications that $Sb_2Mo_{10}O_{31}$ cannot be formed by direct reaction of the pure oxides [3,4]. Moreover, $Sb_2Mo_{10}O_{31}$, as well as other mixed Sb–Mo–O oxides (Sb_2MoO_6 and $Sb_4Mo_{10}O_{31}$), have been synthesized and tested in the same conditions of reactions. It turned out that they were weakly selective to methacrolein. They can thus not explain the improvement of selectivity to methacrolein detected with the mixture of MoO_3 with α-Sb_2O_4 [19].

The catalytic activity as well as the stability of Mo_8O_{23} in the present conditions of reaction has not yet been ascertained. There is still some uncertainty whether the 2 new XRD lines matching the Mo_8O_{23} standard pattern which are detected in the mechanical mixture after the reaction, really correspond to this phase. Even if we have to conclude later that this is the case, it is striking that this phase only appears when antimony oxide is present and not when MoO_3 is tested alone. If this Mo_8O_{23} indeed appears, its formation should be attributed to the action of α-Sb_2O_4 or to the changes it triggers which lead to the reconstruction of the crystallite surface.

Regarding the reconstruction of the crystallites of MoO_3 in the conditions of reaction when α-Sb_2O_4 is present, this modification could in principle have additional consequences concerning the XRD pattern. As (100) structures are created to the detriment of (010) structures, this should theoretically lead to an increase of the $\Sigma\ I_{h00}/\Sigma\ I_{0k0}$ ratio calculated from the XRD peaks of MoO_3 in the mechanical mixture after the reaction. Such an effect, however, was not observed. This is very probably due to the fact that the reconstruction corresponds to relatively microscopic changes. The attenuation of reflections due to the extension of the (100) faces at the expense of the (010) faces could only be detected if the number of stacked crystallographic planes diminished to just a few ones. In the present case, SEM does not suggest such a situation. It is therefore logical that the crystallographic changes observed by SEM cannot be detected in our XRD measurements because they are too small.

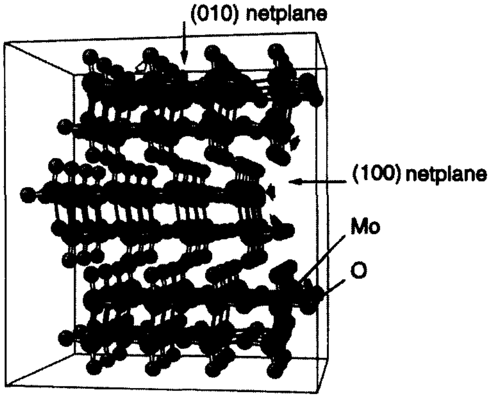
Supposing that Mo_8O_{23} is really in the mixture after the reaction, two hypothesis can be proposed to explain its origin. The first one would be to argue that, in the condition of reaction, the α-Sb_2O_4 has a tendancy to form a hypothetical more stable antimony oxide phase with a higher Sb oxidation state, or to undergo a reduction–reoxidation cycle because of its contact with the reacting mixture of gases. It could be imagined that the oxygen atoms necessary for these oxidation processes are ''pumped'' out of the MoO_3 structure. This would consequently be slightly reduced in a phase as Mo_8O_{23}. Evidences from previous investigations of the MoO_3/α-Sb_2O_4 catalytic system lead to discard this possibility. (i) α-Sb_2O_4 has never been reported to be subject to a reduction–oxidation cycle. There is no indication neither that it be unstable in the conditions of reaction. No other antimony oxide phase than α-Sb_2O_4 has been found in the catalyst after the reaction. (ii) Several experiments with labelled ^{18}O have shown a migration of oxygen from the α-Sb_2O_4 phase to the molybdenum oxide. A migration in the opposite direction has never been observed in the presence of oxygen. (iii) When previously slightly reduced, MoO_3 reoxidizes more rapidly in the presence of α-Sb_2O_4 than alone, confirming that it tends to receive oxygen, rather than to give it to α-Sb_2O_4 [3,7,8,20].

A second more likely hypothesis can be proposed. Mo_8O_{23} could correspond to very local structures, namely ''substructures'', appearing in the zones where the reconstruction was occurring at the moment the reaction was interrupted and the sample cooled, for example at the new edges created between the unreconstructed parts of (010) faces and the newly obtained (100) steps. If one tries to imagine how the reconstruction proceeds "step by step", it is logical to admit that some old (010) crystallographic planes, reorganized as (100) planes, present very locally some stacked crystallographic planes which are no more typical of MoO_3, but of Mo_8O_{23}. The fact that only 2 peaks of Mo_8O_{23} standard pattern have been found by XRD supports that hypothesis. If Mo_8O_{23} was formed as a real new bulk phase, all the peaks, or at least more than 2, of its standard pattern would have been detected (the main peaks missing are $2\theta = 14.3°$, 21°, 22.4°, 31.5°, 34.3°, 44.7°, 46.9°, 47.9°, 52.2°, 57.3°, 60.1°).

This view is not in contradiction with the crystallographic investigation of the very similar $Mo_{18}O_{52}$ phase by Bertrand et al., and by Volta et al.. The $Mo_{18}O_{52}$ structure is described as composed of some strips presenting all the MoO_3 crystallographic characteristics, connected by some overlayings of crystallographic planes which are different from the ones of MoO_3. These connections, what we could call "substructures", correspond to the apparition of the XRD peaks typical of $Mo_{18}O_{52}$ [21,22]. Similar pictures have been shown for Mo_8O_{23} and Mo_9O_{26} by Magnéli, Kilhborg et al., and by Gai et al. [23–25].

The other result of our investigation is firmly established by our SEM picture. This is the formation of steps. This result is quite spectacular. This necessarily explains at least part of the observed increase of catalytic activity and selectivity. As the (100) faces are reported to be selective in partial oxidation, it can be concluded than the creation of selective sites on MoO_3 in the mechanical mixture corresponds to the creation of selective (100) steps by reconstruction of non selective (010) faces. This leads to the enhancement of the selectivity to methacrolein observed in the mechanical mixture. This picture is not in contradiction with the existing literature. Volta et al have shown bulk $Mo_{18}O_{52}$ to be highly selective for the oxidation of propylene to acrolein [22]. As already mentioned, $Mo_{18}O_{52}$ exhibits a structure very similar with the one of MoO_3, with some "accidents" in the crystallographic planes stacking. As a consequence of these accidents, the (010) face of $Mo_{18}O_{52}$ crystallites is composed of (010) terraces with several (100) ledges and (001) kinks, all presenting MoO_3 characteristics. This representation is very close to that which could be proposed for our reconstructed MoO_3 crystals and fits perfectly with our explanation of the catalytic results.

The reconstruction of MoO_3 crystallites only occurred in the presence of α-Sb_2O_4, namely when the surface of MoO_3 was irrigated with spillover oxygen. Strong evidences of this migration have been shown in several publications by labelled ^{18}O experiments [7,8,20]. This shows that this reconstruction is triggered by the reaction of O_{so} with the (010) face of MoO_3. At this stage of the investigation, it is only possible to speculate about how O_{so} does trigger the recon-



Molybdenum trioxide, MoO_3

Fig. 6. Schematic representation of the (010) and (100) faces of MoO_3 crystallites. Hollowed big arrow indicates a Mo atom with the coordination typical of (010). The 4 filled big arrows indicate a group of 4 Mo atoms typical of (100). The figure has been produced with the help of BALSAC software developed by K. Hermann, Fritz-Haber-Institut, Berlin (Germany) [26].

struction. It is supposed that O_{so} would favour the "selective coordination" of Mo atoms or groups of atoms with different coordinations typical of (100). This probably concerns groups of 4 Mo atoms permitting the concerted elimination of 2 hydrogen atoms and the insertion of one oxygen atom into the hydrocarbon molecule. The formation of this selective structure would take place at the expense of the non selective one typical of (010) (namely an arrangement of Mo atoms, all identical in coordination, exhibiting one Mo = O bond and linked together by bridging oxygens). Fig. 6 shows these features for both faces.

5. Conclusion

During the catalytic reaction of mixtures of MoO_3 with α-Sb_2O_4, a partial reconstruction of the non selective (010) face of the molybdenum oxide to selective (100) steps is observed. This does not occur when α-Sb_2O_4 is absent. This phenomenon very likely reflects, at the atomic level, the effects which correspond to the creation of more active and selective sites explaining the synergetic effects observed when MoO_3 is mixed with α-Sb_2O_4. This effect can be attributed to the action of spillover oxygen produced by α-Sb_2O_4 and migrating on the surface of MoO_3. This result is in good agreement with what was theoretically suggested in previous papers [5,6].

As this phenomenon only occurred in the presence of α-Sb_2O_4, this supports the view that the Remote Control Mechanism explains the synergetic effects between antimony and molybdenum oxides in partial oxidation reactions.

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References

[1] R. Castillo, P.A. Awasarkar, Ch. Papadopoulou, D. Acosta and P. Ruiz, in V. Cortes Corberan and S. Vic Bellon, Eds., New Developments in Selective Oxidation II, Elsevier Science B.V., Amsterdam, 1994, p. 795.

[2] E.M. Gaigneaux, P.E. Tsiakaras, D. Herla, L. Ghenne, P. Ruiz and B. Delmon, presented in Catalysis and Photocatalysis on Metal Oxides, ACS Annual Meeting, Chicago, IL, August 21–25, 1995.

[3] (a) B. Zhou, E. Sham, T. Machej, P. Bertrand, P. Ruiz and B. Delmon, J. Catal., 132 (1991) 157; (b) B. Zhou, T. Machej, P. Ruiz and B. Delmon, J. Catal., 132 (1991) 183; (c) F. Melo Faus, Bing Zhou, H. Matralis and Bernard Delmon, J. Catal., 132 (1991) 200.

[4] L.-T. Weng and B. Delmon, Appl. Catal., General, 81 (1992) 141.

[5] B. Delmon, Heter. Chem. Rev., 1 (1994) 219.

[6] B. Delmon, Surf. Rev. Lett., 2(1) (1995) 25.

[7] L.T. Weng, P. Ruiz, B. Delmon and D. Duprez, J. Molecular Catal., 52 (1989) 349.

[8] P. Kaur, D. Martin, D. Duprez, E. Gaigneaux and P. Ruiz. Europacat-II, Maastricht, September 3–8, 1995, p. 162.

[9] L.-T. Weng, B. Zhou, B. Yasse, B. Doumain, P. Ruiz and B. Delmon, 9th Int. Congress on Catalysis. Calgary, Vol. 4, 1988.

[10] P. Ruiz and B. Delmon, Catal. Today, 3 (1988) 199.

[11] C. Li, Q. Xin, P. Ruiz, X.X. Guo and B. Delmon, J. Molec. Catal., 72 (1992) 307.

[12] J.C. Volta, J.M. Tatibouet, C. Phichitkul and J.E. Germain, 8th Int. Congress on Catalysis, Berlin, Vol. 4, 1984, p. 451.

[13] A. Guerrero-Ruiz, J. Massardier, D. Duprez, M. Abon and J.C. Volta, 9th Int. Congress on Catalysis. Calgary, 1988, p. 1601–1608).

[14] B. Mingot, N. Floquet, O. Bertrand, M. Treilleux, J.J. Heizmann, J. Massardier and M. Abon, J. Catal., 118 (1989) 424.

[15] R.A. Hernandez and U.S. Ozkan, Ind. Eng. Chem. Res., 29 (1990) 1454.

[16] M.R. Smith and U.S. Ozkan, J. Catal., 141 (1993) 124.

[17] K. Brückman, R. Grabowski, J. Haber, A. Mazurkiewicz, J. Sloczynski and T. Wiltowski, J. Catal., 104 (1987) 71.

[18] J.C. Volta and J.M. Tatibouet, J. Catal., 93 (1985) 467.

[19] E.M. Gaigneaux, P. Ruiz and B. Delmon, (accepted for poster for 11th Int. Congress on Catalysis, Baltimore, MD, June–July 1996).

[20] (a) G. Mestl, P. Ruiz, B. Delmon and H. Knözinger, J. Phys. Chem., 98 (1994) 11269; (b) G. Mestl, P. Ruiz, B. Delmon

and H. Knözinger, J. Phys. Chem., 98 (1994) 11276; (c) G. Mestl, P. Ruiz, B. Delmon and H. Knözinger, J. Phys. Chem., 98 (1994) 11283.
[21] O. Bertrand, N. Floquet and D. Jacquot, Surface Science, 164 (1985) 305.
[22] J.C. Volta, O. Bertrand and N. Floquet, J. Chem. Soc. Chem. Commun. (1985) 1283.
[23] L. Kihlborg, Acta Chemica Scandinavica (1959) 954.
[24] J. Haggin, C and EN, July 24 (1995) 39.
[25] A. Magnéli, Acta Chemica Scandinavica (1948) 501.
[26] BALSAC (version 2.0, © Copyright K. Hermann 1991-6).