

# Oxidation of Propene in the Absence of Gaseous Oxygen

## I. Single Metal Oxides

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The oxidation of propene in the absence of gaseous oxygen has been studied on unsupported antimony, bismuth, iron, molybdenum and tin oxides. The study was carried out in a flow reactor by following the distribution of the products and the oxygen consumption. The experimental conditions were: temperature, 450-600°C; C<sub>3</sub>H<sub>6</sub> WHSV, 0.05-4 hr<sup>-1</sup>; C<sub>3</sub>H<sub>6</sub> partial pressure, 60-1000 mbar. The main oxidation products were 1,5-hexadiene, benzene, acrolein and, of course, carbon monoxide and dioxide. The above-mentioned oxides can be classified according to their catalytic behavior as follows: (a) highly active, not selective—Fe<sub>2</sub>O<sub>3</sub>; (b) active and selective—Bi<sub>2</sub>O<sub>3</sub>, MoO<sub>3</sub>; (c) weakly active and selective—Sb<sub>2</sub>O<sub>4</sub>, SnO<sub>2</sub>. The highest selectivity to 1,5-hexadiene was obtained on Sb<sub>2</sub>O<sub>4</sub>, to benzene on Bi<sub>2</sub>O<sub>3</sub> and to acrolein on MoO<sub>3</sub>.

The influence of operative parameters, reduction of the catalyst and the trend towards the different allylic products on the various oxides are discussed.

### NOMENCLATURE

The following parameters were considered in order to express the results:

Sel selectivity and conversion,  
C were defined according to  
Voge and Adams (7);  
 $t_r$  reduction time, i.e., the time  
in minutes during which PR  
was flowed over the cata-  
lyst before the analysis;  
 $\Phi$  propene feed, i.e., the  
amount of PR flowed per  
gram of catalyst at the mo-  
ment of the GC analysis:

$$\Phi = \frac{\text{WHSV}}{60} \times t_r$$

where WHSV expresses  
grams of PR per gram of OC

$R_1$  dimerization selectivity, i.e.,  
the amount of dimerized

allyls (which may eventu-  
ally be cyclized) versus the  
amount of allyls forming  
ACR

$$R_1 = \frac{\text{Sel HEX} + \text{Sel BEN}}{\text{Sel ACR}}$$

$R_2$  allylic selectivity, i.e., the  
ratio between the selectivity  
to allylic compounds (ox-  
idized to ACR, dimerized  
to HEX or cyclized to  
BEN) and the deep oxida-  
tion products (CO and  
CO<sub>2</sub>):

$$R_2 = \frac{\text{Sel HEX} + \text{Sel BEN} + \text{Sel ACR}}{\text{Sel CO} + \text{Sel CO}_2}$$

oxygen consumption, ( $\mu\text{mol m}^{-2}$ ) as a function of  $t_r$ , was  
calculated by integrating  
against time the differential

amounts of consumed oxygen determined through the conversion, the selectivities, and the specific oxygen consumption of every product and the surface area of the catalyst.

## INTRODUCTION

The possibility of selective catalytic oxidation of propene (PR) via allylic intermediates to acrolein (ACR), hexadienes (HEX) and benzene (BEN) has been widely emphasized in the scientific and patent literature (1-4). The solids employed as catalysts are generally composed of one or more oxides of transition metals: in some cases discrete binary or ternary crystalline phases have been detected, whereas in other cases the catalyst is a simple mixture of oxides.

Even if the oxidations are carried out in the presence of air, it has been suggested that the oxidizing species in the system are the oxidic oxygens of the catalyst and that the gasphase oxygen merely replenishes the anion vacancies created by reduction of the catalyst surface. The present study was undertaken to investigate these questions further. Specifically, the work was aimed at finding out the catalytic properties of individual oxides that frequently are present in catalysts for the oxidation and/or ammoxidation of olefins.

To carry out this task, we chose to separate the study of the behavior of the lattice oxygen from the virtually independent phenomenon of the uptake of gas-phase oxygen by the solid during the reoxidation of the catalyst. For this reason we operated in depletive conditions (5,6), i.e., we carried out the oxidation of PR by means of the oxygen of the catalyst itself. We investigated the oxidation of PR on antimony, bismuth, iron, molybdenum and tin oxides, measuring the change of catalytic activity and product distribution as a function of the increasing reduction of the

solids. We also followed by X-ray analysis the structural modifications that occur during the reaction.

## EXPERIMENTAL METHODS

### *Preparation of Oxides*

All catalysts were prepared according to the procedure described below. The final products were pelletized, ground, sieved and the fraction between 50 to 70 mesh was used. Starting materials for the preparation of the catalysts were all reagent grade products.

*Sb<sub>2</sub>O<sub>4</sub>*. Antimony tetroxide was prepared by oxidizing a fine powder (1  $\mu$ m) of Sb<sub>2</sub>O<sub>3</sub> with concentrated HNO<sub>3</sub>. After elimination of the acid, the catalyst was activated up to 600°C. Its BET surface area was 4.3 m<sup>2</sup> g<sup>-1</sup>.

*Bi<sub>2</sub>O<sub>3</sub>*. Bismuth oxide was prepared by hydrolysis with deionized water of a solution of Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O. The precipitate was filtered, washed, dried and activated up to 600°C. The BET surface area of the final catalyst was 0.4 m<sup>2</sup> g<sup>-1</sup>.

*MoO<sub>3</sub>*. Molybdenum oxide was prepared by precipitation with diluted nitric acid of a solution of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O in water and ammonia. The precipitate was filtered, washed, dried and activated up to 600°C. The surface area of the catalyst was 0.6 m<sup>2</sup> g<sup>-1</sup>.

*Fe<sub>2</sub>O<sub>3</sub>*. Iron oxide was prepared by thermal decomposition of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and calcination up to 800°C. The BET surface area was 1.8 m<sup>2</sup> g<sup>-1</sup>.

*SnO<sub>2</sub>*. Tin dioxide was prepared by dissolving (NH<sub>4</sub>)<sub>2</sub>SnCl<sub>6</sub> in deionized water, adding a small amount of HCl and then slowly precipitating with diluted NH<sub>4</sub>OH. The precipitate was washed, dried and then calcined up to 800°C: a BET surface area of 5.3 m<sup>2</sup> g<sup>-1</sup> was obtained.

### *Equipment*

The depletive oxidative dehydrogenation was studied in a flow system at atmospheric pressure. Metered streams of

PR-He, pure PR, pure He and air were dried over molecular sieves and fed to the reactor. The reactor consisted of a quartz tube containing a 2 cm<sup>3</sup> fixed bed of catalyst. Temperatures along the length of the catalytic bed were monitored by means of thermocouples.

Analysis was performed by gas chromatography: columns packed with Porapak Q with a temperature program from 120 to 190°C allowed a complete separation of CO, CO<sub>2</sub>, H<sub>2</sub>O, ACR, HEX and BEN.

Routine analysis did not separate all the hexadienes so that all isomers are indicated by the symbol HEX. However, a complete separation was occasionally performed and it was found that 1,5-hexadiene was the main component (about 90%) with small amounts of 2,4-hexadiene, 1,3-hexadiene, 1,4-hexadiene, 1,3-cyclohexadiene and 1,4-cyclohexadiene. Small amounts (less than 4%) of other aldehydic compounds (acetic and propionic aldehydes) detected in many cases were not considered. The sampling device allowed the analysis both of the feed mixture and of the effluent products.

### Procedure

The catalytic behavior of the oxides was studied in the following range of conditions:

temperature, 450–600°C;

reduction time, 1–30 min;

PR partial pressure, 60 mbar–1 bar (commercial PR > 99.95% mixed with helium > 99.998%);

PR weight hour space velocity, WHSV, 0.05–4 hr<sup>-1</sup>.

The reduction–oxidation cycle performed in all the experiments was:

30 min flushing with a helium stream to remove the residual air;

reduction with PR for different times according to the experiments;

analysis of the effluent products;

30 min flushing with He;

reoxidation with air (> 99.95%) for at least 30 min.

To evaluate the reproducibility of the experiments, after some conditioning cycles, the tests were repeated in the same operative conditions with fairly constant results. In this way, it was proved that reduction–oxidation of the catalysts is a reversible process, at least in the conditions used in our experiments.

## RESULTS

### Depletive Conditions

No substantial qualitative differences of PR conversion as a function of  $t_r$  are detected on the studied oxides by changing the temperature from 450 to 550°C. The conversions at 550°C are shown in Fig. 1. On Bi<sub>2</sub>O<sub>3</sub> and MoO<sub>3</sub> at 550°C high conversions, nearly constant with  $t_r$ , are obtained, without significant variations even if the reduction is such that structural modifications are detected by X-ray diffraction (i.e., presence of metallic Bi and MoO<sub>2</sub>; see Table 1). At 450°C conversions are lower with an initial dependence on  $t_r$ . The behavior of Sb<sub>2</sub>O<sub>4</sub> is similar, but its activity is lower. In the case of Fe<sub>2</sub>O<sub>3</sub>, after a very high initial activity, there is a de-

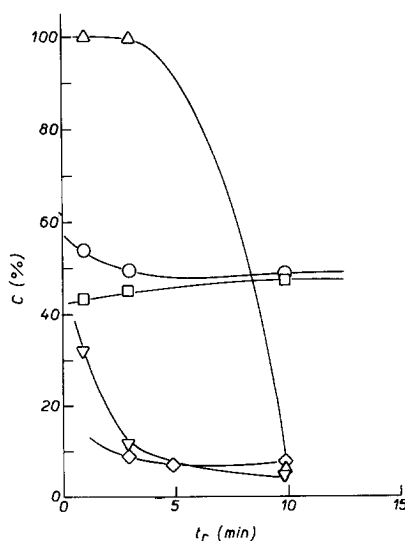


FIG. 1. Values of conversion of PR (108 mb partial pressure) vs  $t_r$  at 550°C: (○) Bi<sub>2</sub>O<sub>3</sub>, (△) Fe<sub>2</sub>O<sub>3</sub>, (□) MoO<sub>3</sub>, (◇) Sb<sub>2</sub>O<sub>4</sub>, (▽) SnO<sub>2</sub>.

TABLE 1  
CATALYST PHASE COMPOSITION FROM  
X-RAY ANALYSIS<sup>a</sup>

Before reduction	After 10 min reduction
$\alpha$ -Bi <sub>2</sub> O <sub>3</sub> + ( $\gamma$ -Bi <sub>2</sub> O <sub>3</sub> )	$\alpha$ -Bi <sub>2</sub> O <sub>3</sub> + (Bi + $\gamma$ -Bi <sub>2</sub> O <sub>3</sub> )
MoO <sub>3</sub>	MoO <sub>3</sub> + (Mo <sub>9</sub> O <sub>26</sub> + MoO <sub>2</sub> )
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	Fe <sub>3</sub> O <sub>4</sub>
Sb <sub>2</sub> O <sub>4</sub> amorphous	$\alpha$ -Sb <sub>2</sub> O <sub>4</sub> + (Sb <sub>2</sub> O <sub>3</sub> + $\beta$ -Sb <sub>2</sub> O <sub>4</sub> + Sb <sub>2</sub> O <sub>4</sub> amorphous)
SnO <sub>2</sub>	SnO <sub>2</sub>

<sup>a</sup> Parentheses indicate that only small amounts were present.

crease of conversion, corresponding to the formation of Fe<sub>3</sub>O<sub>4</sub> (Table 1). The trend on SnO<sub>2</sub> is a decreasing activity with a high initial conversion and without detectable structural changes.

The selectivities to the main oxidation products, at 550°C, against the reduction time, are displayed in Figs. 2, 3 and 4. It is evident that for every product there is an oxide showing a far better selectivity (Sb<sub>2</sub>O<sub>4</sub> for HEX, Bi<sub>2</sub>O<sub>3</sub> for BEN and MoO<sub>3</sub> for ACR). It may be pointed out

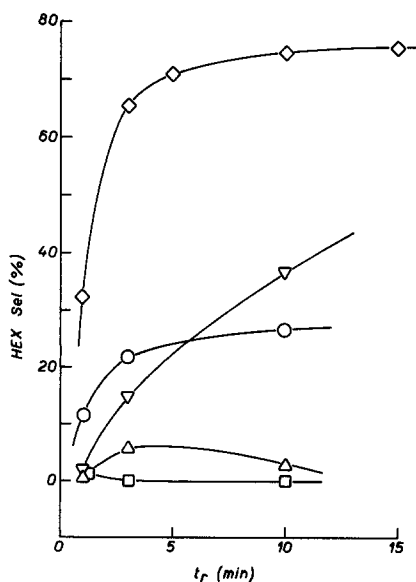


FIG. 2. Values of selectivity to HEX vs  $t_r$  at 550°C: (○) Bi<sub>2</sub>O<sub>3</sub>, (△) Fe<sub>2</sub>O<sub>3</sub>, (□) MoO<sub>3</sub>, (◇) Sb<sub>2</sub>O<sub>4</sub>, (▽) SnO<sub>2</sub>.

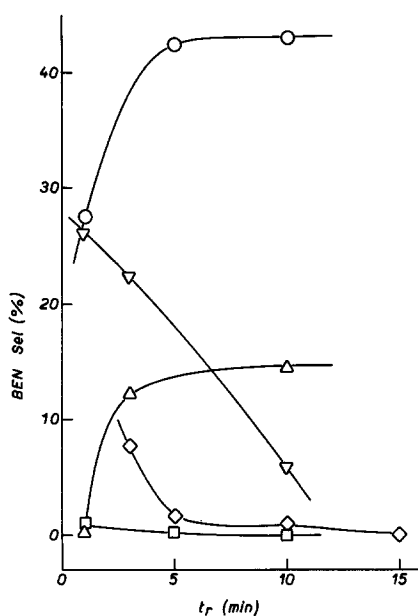


FIG. 3. Values of selectivity to BEN vs  $t_r$  at 550°C: (○) Bi<sub>2</sub>O<sub>3</sub>, (△) Fe<sub>2</sub>O<sub>3</sub>, (□) MoO<sub>3</sub>, (◇) Sb<sub>2</sub>O<sub>4</sub>, (▽) SnO<sub>2</sub>.

that after the first minute, the sum of the selectivities to HEX and BEN is nearly independent of the reduction time.

On MoO<sub>3</sub> ACR is the only selective prod-

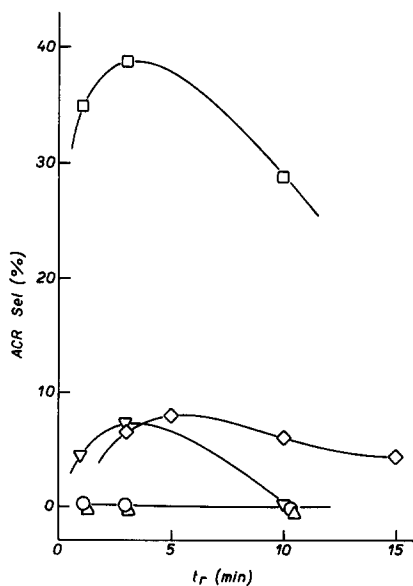


FIG. 4. Values of selectivity to ACR vs  $t_r$  at 550°C: (○) Bi<sub>2</sub>O<sub>3</sub>, (△) Fe<sub>2</sub>O<sub>3</sub>, (□) MoO<sub>3</sub>, (◇) Sb<sub>2</sub>O<sub>4</sub>, (▽) SnO<sub>2</sub>.

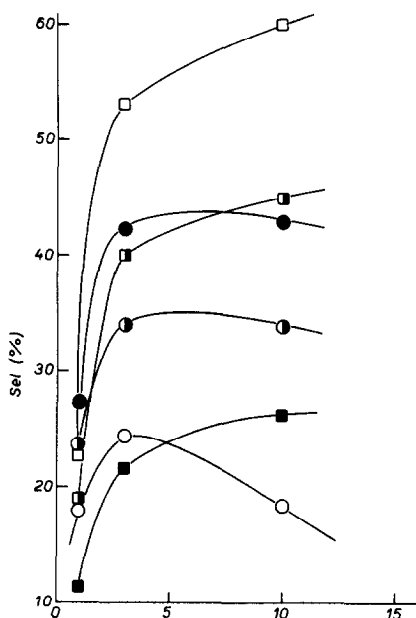


FIG. 5. Values of selectivities vs  $t$ , on  $\text{Bi}_2\text{O}_3$  at different temperatures ( $^{\circ}\text{C}$ ): to HEX: 450 ( $\square$ ), 500 ( $\square$ ), 550 ( $\blacksquare$ ); to BEN: 450 ( $\circ$ ), 500 ( $\bullet$ ), 550 ( $\bullet$ ).

uct whereas on  $\text{Bi}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  only traces of ACR are obtained.

The influence of temperature on selectivities in the case of  $\text{Bi}_2\text{O}_3$  is given in Fig. 5: by raising the temperature the selec-

tivity towards BEN increases while the selectivity to HEX decreases.

The influence of the partial pressure of PR was studied as a function of  $\Phi$  on  $\text{Sb}_2\text{O}_4$ . The selectivity to allylic compounds at various PR partial pressures is displayed in Fig. 6, where  $R_2$  is plotted against  $\Phi$  for three different pressures: as shown, allylic selectivity increases at the higher PR pressures. The dimerization selectivity  $R_1$  follows a similar trend, as shown in Fig. 7, where the values obtained at four different PR partial pressures are plotted against  $\Phi$ .

As might be expected, conversion increases with PR partial pressure and decreases with WHSV; in both cases an increased reduction of the catalyst causes a lower conversion. On the other hand, the selectivities to ACR, HEX, BEN studied at constant reduction time are not affected by WHSV.

#### Non-depletive Conditions

One set of experiments was performed on  $\text{Sb}_2\text{O}_4$  and  $\text{Bi}_2\text{O}_3$  at  $550^{\circ}\text{C}$  and atmospheric pressure in the presence of oxygen, ( $>99.95\%$ ) with a feed ratio  $\text{C}_3\text{H}_6:\text{O}_2:\text{He} = 1:0.4:16.6$  and a PR WHSV of  $100 \text{ hr}^{-1}$ .

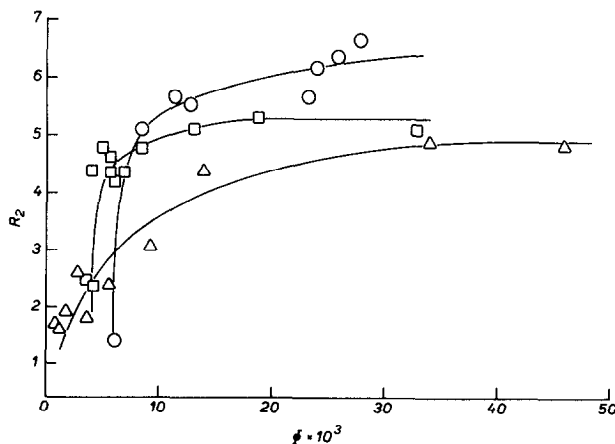


FIG. 6. Values of  $R_2$  vs  $\Phi$  at  $550^{\circ}\text{C}$  at different PR partial pressures (mbar): on  $\text{Sb}_2\text{O}_4$ : 61 ( $\Delta$ ); 108 ( $\square$ ); 376 ( $\circ$ ).

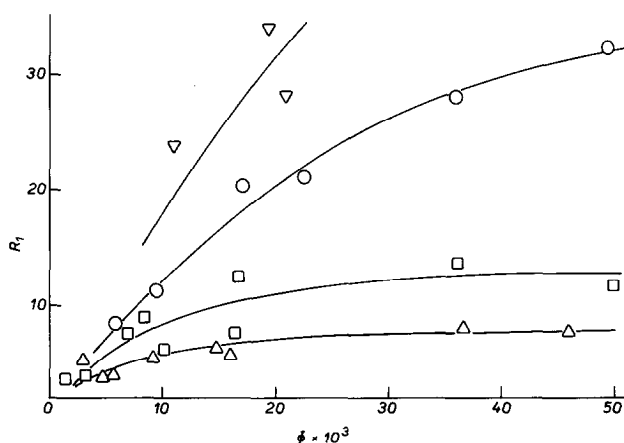


FIG. 7. Values of  $R_1$  vs  $\Phi$  at 550°C at different PR partial pressures (mbar): on  $\text{Sb}_2\text{O}_4$ : 61 ( $\Delta$ ); 108 ( $\square$ ); 376 ( $\circ$ ); 1013 ( $\nabla$ ).

Conversions around 11% were obtained on  $\text{Sb}_2\text{O}_4$ ; in comparison to the results found in depletive conditions there was a slight decrease in partial oxidation products, without significant changes of the ratio HEX:BEN and with a decrease of  $R_1$  (i.e., more ACR).

The results obtained on  $\text{Bi}_2\text{O}_3$  were similar to those of Swift *et al.* (5) in the presence of air; however, small amounts of acrolein were produced. In comparison to the depletive conditions, lower allylic selectivity was found without changes in HEX:BEN ratio.

## DISCUSSION

The catalytic behavior of metallic oxides in various oxidation reactions has been the object of many studies and consequently several classifications have been proposed.

For propene oxidation, the oxides considered here were regarded by Seiyama *et al.* (8) as ACR formers ( $\text{MoO}_3$ ,  $\text{Sb}_2\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ ) and HEX or Ben formers ( $\text{Bi}_2\text{O}_3$ ,  $\text{SnO}_2$ ). The behavior was interpreted on the basis of the electronegativity of the metal ion. Our results (obtained in oxygen depletive conditions, whereas Seiyama *et al.* worked in the presence of gas-phase oxygen) differ from this classification particularly because  $\text{Fe}_2\text{O}_3$  must be essen-

tially considered a carbon dioxide former and  $\text{Sb}_2\text{O}_4$  a HEX and BEN former. For  $\text{Bi}_2\text{O}_3$  our results agree with the recent literature (5,8), but there are discrepancies with respect to earlier data according to which the oxide was considered a carbon dioxide former (9) or an acrolein former (15). The selectivities we found were higher than those of Seiyama *et al.* (8) and this could be ascribed to the lower probability of a deep degradation of PR in depletive conditions.

On the basis of the total selectivity to allylic compounds with respect to the deep oxidation we could consider that:

- $\text{Fe}_2\text{O}_3$  is highly active, but not selective (conversion greatly dependent on  $t_r$ )
- $\text{Bi}_2\text{O}_3$  and  $\text{MoO}_3$  are active and selective (conversion nearly independent of  $t_r$ )
- $\text{Sb}_2\text{O}_4$  and  $\text{SnO}_2$  are weakly active and selective (conversion independent of  $t_r$  for the former and dependent on  $t_r$  for the latter).

A useful way to interpret the different activities could be to compare oxygen consumption (OC) (Fig. 8) and oxygen availability on the catalytic surface, calculated to be  $9.38 \mu\text{mol}(\text{O}_2) \text{m}^{-2}$  for all the oxides on the average (10,11). From this comparison a very significant evaluation of the activity of the oxygen on the surface and

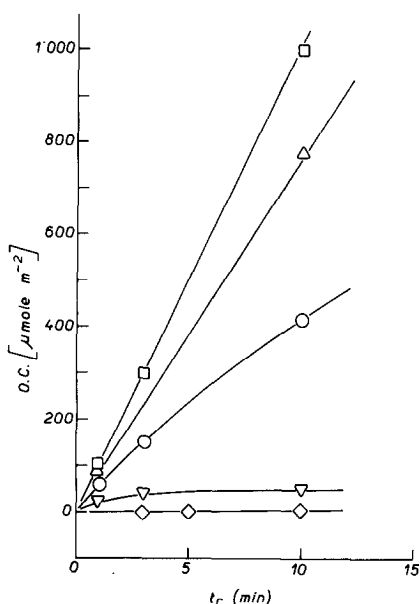


FIG. 8. Values of oxygen consumption at 550°C vs  $t_r$  on:  $\text{Bi}_2\text{O}_3$  (○);  $\text{Fe}_2\text{O}_3$  (△);  $\text{MoO}_3$  (□);  $\text{Sb}_2\text{O}_4$  (◇);  $\text{SnO}_2$  (▽).

the importance of the oxygen diffusion from bulk to surface may be obtained. In the case of  $\text{Sb}_2\text{O}_4$  the oxygen consumed during the considered reaction time is less than the oxygen available on the surface and this explains the independence of conversion from  $t_r$ : no bulk oxygen is involved in the reaction and the oxidation may be ascribed to the surface oxygen which reacts according to a single mechanism.  $\text{SnO}_2$  behaves differently because all the surface oxygen is consumed in a few minutes with a remarkable conversion of PR. Afterwards there is a sharp decrease of activity and the low subsequent conversion may be ascribed to the slow oxygen diffusion from bulk to surface. Such a diffusion would be the rate determining step on the reduced catalyst. For bismuth, iron and molybdenum oxides, the OC by the first minute is greater than the surface oxygen so that bulk oxygen is consumed and the reaction occurs easily owing to the high oxygen mobility from bulk to surface.

Oxygen mobility in these oxides was

studied by thermogravimetric measurements (12) and by isotopic exchange (10,13). The results of depletive oxidation of propene, which can be considered an indirect measurement of such a mobility, are in good agreement with the above studies.

The structural modifications occurring during the reaction were followed by X-ray analysis: only traces of reduced phases were detected, with the exception of  $\text{Fe}_2\text{O}_3$  which undergoes a complete transformation to the phase  $\text{Fe}_3\text{O}_4$ , which has a slightly lower O/Fe ratio (Table 1).

The possibility of interpreting the selectivity to allylic compounds of a catalyst is widely discussed in the literature but a satisfactory pattern is still lacking.

Trimm and Doerr (14), studying the oxidation of PR on  $\text{In}_2\text{O}_3$ , found that ACR and HEX are the initial products of reaction, their formation being concurrent but independent, whereas BEN is formed from HEX, the last reaction being accelerated by the temperature. Our results, showing (see for instance Fig. 5) that the sum of HEX and BEN is nearly constant with  $t_r$  and with the temperature and that the ratio HEX:BEN decreases with the temperature, fit very well into the above pattern.

The change of selectivities with  $t_r$  could be connected to the different oxygen availability on the surface. At the beginning there is a high density of oxygen atoms on the surface so that a complete oxidation of PR is favored. The subsequent formation of anion vacancies and the lower probability of finding contiguous sites occupied by oxygen facilitate the oxidative dehydrogenation to an allylic intermediate. When the surface is further depleted, the probability of the interaction of two allyls increases in comparison to the probability of the oxidation of a single allyl to ACR. The increase of  $R_1$  by raising the PR partial pressure (Fig. 7) could be ascribed, in the same way, to the greater probability of interaction between two allyls.

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