JOURNAL OF CATALYSIS **146**, 126–135 (1994)

Structural, Surface, and Catalytic Properties of Bismuth Molybdovanadates Containing Foreign Atoms

V. Oxidative Dehydrogenation of 1-Butene on Iron-Containing Bismuth Molybdovanadate Catalysts

S. De Rossi,[1] M. Lo Jacono, M. Gardini,† and P. Porta

Centro di Studio su "Struttura e Attività Catalitica di Sistemi di Ossidi" (SACSO) del CNR, c/o Dipartimento di Chimica, Università di Roma "La Sapienza," Piazzale Aldo Moro 5, 00185 Rome, Italy

Received December 2, 1992; revised April 8, 1993

The oxidative dehydrogenation of 1-butene has been studied over catalysts with the scheelite structure and general formula $Bi_{1-x/3}\square_{x/3-y}Me_y[V_{1-x}Mo_{x-y}Fe_y]O_4$ with $x = 0.45$; $y = 0$, 0.10, or 0.15; Me = Fe or Bi. Experiments were carried out in a pulse microreactor in the temperature range 473–673 K. The trend of total conversion with catalyst composition is similar to that found previously for the same catalysts in propene oxidation. Moreover, the total conversion was identical in the presence and in the absence of gaseous oxygen in the pulse (first pulse with 1-butene alone). On the other hand, the production of butadiene was markedly different from that of acrolein in the propene reaction for the catalyst in which the cationic vacancies were completely filled with bismuth ions ($y = 0.15$, Me = Bi). This finding points to a differing importance of the cationic vacancies depending on whether the selective reaction occurs with oxygen insertion. Also the oxidation to isomerization ratios and the reduction–oxidation properties changed with catalyst composition. The results are discussed in terms of participation of cationic vacancies and iron ions in the steps of the allylic oxidation. © 1994 Academic Press, Inc.

INTRODUCTION

Iron-containing bismuth molybdovanadates with the scheelite structure (ABO_4) and general formula $Bi_{1-x/3}\square_{x/3-y}Me_y[V_{1-x}Mo_{x-y}Fe_y]O_4$ with Me = Fe or Bi have been the object of a series of papers dealing with the structural, surface, and catalytic properties of the system (1–5). The study of the oxidation of propene to acrolein (2) on four groups of catalysts, namely, those with $x = 0.45$ and $x = 0.60$ with either Me = Fe or Me = Bi, showed that the presence of cationic vacancies in the catalyst structure was beneficial, in agreement with the results presented by Sleight (6). Moreover, iron was found to play a positive role in reducing the activation energy of the process and increasing the selectivity to acrolein, at least in the presence of cationic vacancies. The importance of the eight-coordinated A site in bonding the olefin was also pointed out. An XPS study from our laboratory (5) has indeed supported the view that propene interacts preferentially with the Bi^{3+} ions, in agreement with the mechanism proposed by Haber and co-workers (7, 8).

In order to gain further information on the relationship between catalytic properties in allylic oxidation and the role of the catalyst components in the iron-containing Bi–Mo–V oxide system, a study of the oxidative dehydrogenation of 1-butene to 1,3-butadiene (hereinafter simply designated as butadiene) has been undertaken. This reaction has been widely studied in the past over numerous oxidic systems (9–12) and particularly on Bi–Mo-containing catalysts (7, 13–17). Scheelite systems have also been investigated by Linn and Sleight (18), and some parameters controlling the selectivity in butene oxidation on molybdate catalysts have been discussed by Centi and Trifirò (19). The properties of ferrite catalysts in the butene reaction have been reviewed by Kung and Kung (20).

The oxidative dehydrogenation of butene is particularly significant for our investigation of the Fe–Bi–Mo–V oxide system since it possesses some analogies and some differences with the propene oxidation already studied (2). The main analogy resides in a common first step consisting of an α-hydrogen abstraction and allyl formation, which are generally considered to be rate determining. The differences are mainly the additional parameter of double-bond isomerization of the reactant olefin and the absence of oxygen insertion into the product of selective oxidation.

Thus the aims of the present work were: (i) to study the

---

[1] To whom correspondence should be addressed.

† Deceased. To whom this paper is dedicated.

0021-9517/94 $6.00

catalytic behavior of the catalysts in relation to their composition, (ii) to compare this behavior with that found in propene oxidation, (iii) to follow the distribution of the products during the reduction of the catalyst by the hydrocarbon, and (iv) to study the reoxidation of the reduced catalysts. To this end we chose to employ the pulse technique, as in the preceding investigation (2). Pulse experiments, though not very suitable for studies of kinetics because of the absence of a steady state, nevertheless offer the possibility of investigating the catalytic properties of the active surface when it first encounters the reactant(s) and are suitable for separately studying the reduction and the reoxidation of the catalyst.

EXPERIMENTAL

Catalysts

The catalysts used were some of those previously investigated for the propene oxidation (2). They are listed in Table 1 together with their BET surface areas, which because of their low values were measured using krypton (σ = 0.196 nm^2). Since, with reference to the general formula reported above, they all have $x = 0.45$, a specimen is indicated hereafter simply by the value of y (0, 0.10, or 0.15) and specifying *Me* (Fe or Bi).

Details on the preparation and characterization of these samples by various techniques have been reported elsewhere (1, 3–5). Here it is sufficient to recall that all catalysts were monophasic with the scheelite structure and that, by increasing the value of y from 0 to $x/3$, iron substitutes for molybdenum or vanadium in the tetrahedral *B* sites of the scheelite structure. In the samples with *Me* = Fe, iron also replenishes the eight-coordinated *A* vacancies, whereas in the specimens with *Me* = Bi, these vacancies are progressively filled by Bi^{3+} ions.

Procedure

Activity measurements. Catalytic tests were performed in the temperature range 473–673 K by the pulse technique and using 1.0 g of powdered catalyst, contained in a pyrex reactor vertically positioned in an electrical oven. Temperature control within ±1 K was obtained with a commercial device. All the experiments were carried out in the same apparatus employed to study the propene oxidation (2). High-purity gases were used. Helium (Matheson UHP) was employed as carrier of the pulses. 1-Butene (Matheson CP) and oxygen (SIO 99.95%) were submitted to double distillation before use as reactants.

TABLE 1

Nominal Composition and Surface Areas of the Examined Catalysts: $Bi_{1-x/3}\,\square_{x/3-y}Me_y[V_{1-x}MO_{x-y}Fe_y]O_4$ with $x = 0.45$

y	*Me*	Nominal formula	Surface area (m^2 g^{-1})
0.00	—	$Bi_{0.85}\,\square_{0.15}[V_{0.55}Mo_{0.45}]O_4$	0.7
0.10	Fe	$Bi_{0.85}\,\square_{0.05}Fe_{0.10}[V_{0.55}Mo_{0.35}Fe_{0.10}]O_4$	1.5
0.15	Fe	$Bi_{0.85}Fe_{0.15}[V_{0.55}Mo_{0.30}Fe_{0.15}]O_4$	2.0
0.10	Bi	$Bi_{0.95}\,\square_{0.05}[V_{0.55}Mo_{0.35}Fe_{0.10}]O_4$	0.8
0.15	Bi	$Bi_{1.00}[V_{0.55}Mo_{0.30}Fe_{0.15}]O_4$	3.8

The composition of the pulse was varied according to the scope of the experiment. Indeed, pulses containing a mixture of oxygen and 1-butene (3.5 μmol of O_2 + 3.5 μmol of 1-C_4H_8 in each pulse) were used in order to compare the activity trends with those found in the propene oxidation, where this mixture had been employed. Pulses of 1-butene alone (3.5 or 5 μmol per pulse) were used to compare experiments without oxygen with those in the presence of oxygen and to study the distribution of the reaction products resulting from the catalyst reduction, as well as to investigate the catalyst reduction itself. The 1-butene-containing pulses were passed through the catalyst every 50 min, this interval of time being that required for a complete GC analysis. The flow rate of the carrier He was 25 ± 1 cm$^3_{STP}$ min^{-1} in all experiments.

Before a series of pulses with 1-butene, the catalyst was pretreated with a flow of oxygen overnight at 723 K in order to burn out carbonaceous contaminants possibly remaining from preceding experiments. The catalyst was then equilibrated in a helium flow at 723 K for 30 min. The latter treatment had a slight reducing effect, which was, however, negligible compared with that produced by the pulses of hydrocarbon. The above standard conditioning, even when repeated several times, gave rise to a satisfactorily reproducible surface from the point of view of the catalytic properties. In fact, the reproducibility for either total conversion or yields to the various products was generally ±3% of the measured value.

Catalyst reoxidation. The reoxidation properties of the catalysts were studied at different temperatures on sample portions always prereduced to the same extent of reduction with one pulse of 1-butene (5 μmol) at 673 K. The helium flow followed the 1-butene pulse for about 30 min, during which the temperature was adjusted to the desired value for the reoxidation experiment (at least three different temperatures for each catalyst).

Oxygen pulses (5 μmol each) were then passed over the reduced catalyst at intervals of 15 min and the amount of oxygen taken up was evaluated. Allowance was made for the CO_2 produced during the reoxidation, due to carbon-containing species left on the surface during the 1-butene pulse. In the calculation, the carbonaceous residue was considered to have the same carbon/hydrogen ratio as butadiene. It is noted that at 673 K the amount of oxygen consumed to burn the residue was less than 5% of the total oxygen consumption.

GC analysis. The gas-chromatographic analysis was generally performed in two steps. All compounds, except permanent gases, were collected at the exit of the reactor for 10 min in a trap held at 77 K, while oxygen (when present) and CO were analyzed in a 1-m, 4-mm-i.d. column filled with molecular sieve 5A held at 393 K. Then, by a rapid warming of the trap, the condensed compounds were flashed into a 5-m, 4-mm-i.d. column filled with 20% dimethylsulfolane supported on Chromosorb P held at 273 K. The latter column allowed the separation of CO_2, 1-butene, *trans*-2-butene, *cis*-2-butene, and butadiene. The areas of the peaks were determined by an integrator (Hewlett–Packard 3370A). The accuracy of the gas-chromatographic analysis was within ±0.05 μmol for all compounds.

Data treatment. The total percentage conversion, C, the percentage yield of a product i, Y_i, and its percentage selectivity, S_i, are defined in the usual manner as

$$C = 100 \times [(\mu\text{mol of 1-butene})_{\text{in}} - (\mu\text{mol of 1-butene})_{\text{out}}]/(\mu\text{mol of 1-butene})_{\text{in}} \quad [1]$$

$$Y_i = 100 \times \mu\text{mol of } i \times n_i/\,(\mu\text{mol of 1-butene})_{\text{in}} \quad [2]$$

$$S_i = 100 \times \mu\text{mol of } i \times n_i/[(\mu\text{mol of 1-butene})_{\text{in}} - (\mu\text{mol of 1-butene})_{\text{out}}], \quad [3]$$

where n_i is $\frac{1}{4}$ of the carbon atoms of the product i.

The amount of oxygen lost, O_L, by the catalyst during passage of the pulses of 1-butene has been evaluated by the reactions

$$1\text{-}C_4H_8 + O_L \rightarrow C_4H_6 + H_2O$$

$$1\text{-}C_4H_8 + 8O_L \rightarrow 4CO + 4H_2O$$

$$1\text{-}C_4H_8 + 12O_L \rightarrow 4CO_2 + 4H_2O.$$

Then,

$$\text{total } O_L\ (\mu\text{mol of atoms}) \text{ in a pulse} = \mu\text{mol of } C_4H_6 + 2 \times \mu\text{mol of CO} + 3 \times \mu\text{mol of } CO_2. \quad [4]$$

At 673 K a few percent of furan was present in the reaction products. In these circumstances, the stoichiometric amount of oxygen consumed for furan formation was taken into account in the calculation of the oxygen lost.

RESULTS

Preliminary Tests of Activity

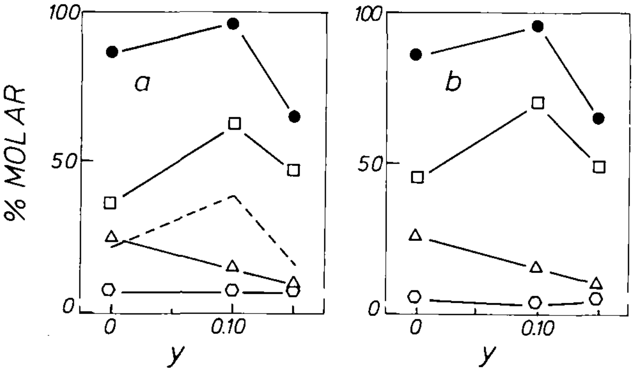

FIG. 1. Oxidative dehydrogenation of 1-butene on $Bi_{0.85}\,\square_{0.15-y}\,Me_y[V_{0.55}Mo_{0.45-y}Fe_y]O_4$. Reaction temperature: 623 K. Pulse composition: (a) 3.5 μmol of 1-butene + 3.5 μmol of O_2 and (b) 3.5 μmol of 1-butene. (●) Total conversion, (□) butadiene, (△) 2-butenes, (○) $(CO + CO_2)/4$, and (---) propene conversion from Ref. (2).

Initial experiments were carried out over three catalysts, namely, $y = 0$ (without iron), $y = 0.10$ with Me = Bi, and $y = 0.15$ with Me = Bi. The results at the reaction temperature 623 K are shown in Fig. 1, where the total conversion of the 1-butene and the yields of butadiene, *cis*- and *trans*-2-butene isomers, and carbon oxides are reported vs the composition parameter y of the catalysts. Figure 1a shows the results obtained using pulses of mixed oxygen and 1-butene (average values from three pulses), and Fig. 1b shows the results with pulses of 1-butene alone (data referring to the first pulse on each catalyst after standard pretreatment). The propene conversion previously measured (2) at the same reaction temperature and with an analogous hydrocarbon plus oxygen composition of the pulse is reported for comparison as a dotted line in Fig. 1a.

It is to be noted that (i) the 1-butene conversion is identical in the presence or in the absence of gaseous oxygen in the pulse over all the catalysts and (ii) the trend of the 1-butene conversion parallels that already found for the propene conversion in the previous study on the same catalysts. The conversions measured for the 1-butene reaction are, however, significantly higher than those of the propene at the same temperature, a result expected on the basis of the known different reactivity of the two hydrocarbons (13).

The results indicate that the main reaction is virtually unaffected by the presence of gaseous oxygen and give support to the view that lattice oxygen participates in the oxidation process, according to a classical Mars–van Krevelen redox mechanism (21) in which the role of the gaseous oxygen is to regenerate the reduced catalyst in a subsequent reaction step. This mechanism seems to apply also to the production of the carbon oxides, which is only marginally increased by the presence of gaseous oxygen in the pulse.

1-Butene Dehydrogenation

On the basis of the above findings, the succeeding more systematic experiments were carried out using pulses of

1-butene alone with the aim of studying the catalytic behavior during the reduction of the samples. To this end, five pulses of 1-butene were passed over each of the five catalysts under investigation at a given temperature. The results are illustrated in Figs. 2, 3, and 4 for experiments at 673, 573, and 473 K, respectively. It is apparent that definite orders of activity (total conversion per g) exist independently of the reaction temperature, i.e., for *Me* = Fe (y = 0.15) ≥ (y - 0.10) > (y = 0) and for *Me* = Bi (y = 0.15) < (y = 0.10) > (y = 0). This trend, which is better observable at the lower temperature (473 K), once again very closely resembles that found in the previously studied oxidation of propene on the same catalysts (2).

At 673 K (Fig. 2) the major product is butadiene (accompanied by some CO and CO_2) with minor amounts of isomers, while the reverse occurs at 473 K (Fig. 4). An intermediate situation is observed at 573 K (Fig. 3). To provide better evidence for this general trend, Fig. 5 shows the temperature effect on the selectivities to various reaction products for the catalyst y = 0.10 with *Me* = Fe.

With regard to the trends of the conversion and the yields of the reaction products with the number of pulses (catalyst reduction), it is apparent from the total conversion data in Fig. 2 that, at high temperature (673 K), there is very little activity decay, but it is more pronounced for

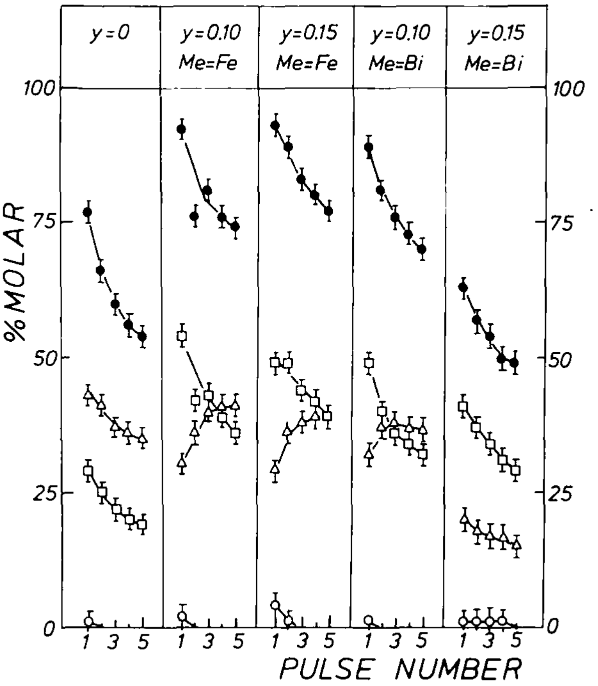

FIG. 3. Oxidative dehydrogenation of 1-butene on $\text{Bi}_{0.85}\square_{0.15-y}Me_y[\text{V}_{0.55}\text{Mo}_{0.45-y}\text{Fe}_y]\text{O}_4$. Reaction temperature: 573 K. Pulse composition and symbols as in Fig. 2.

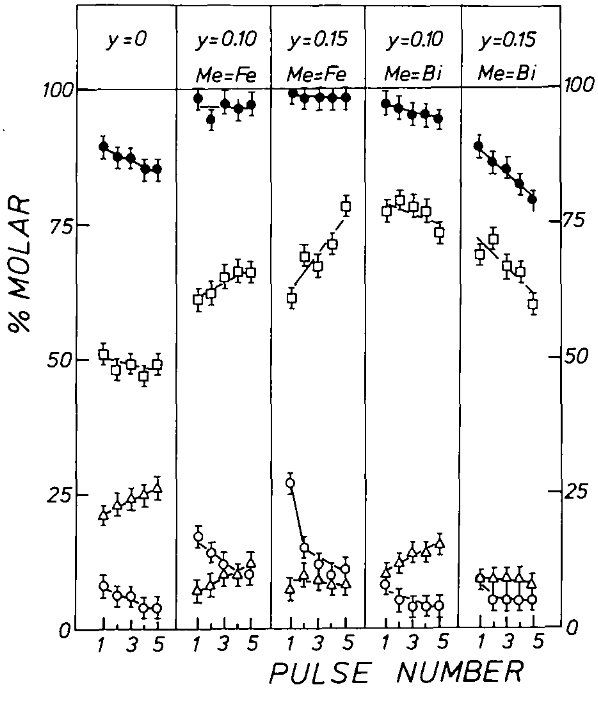

FIG. 2. Oxidative dehydrogenation of 1-butene on $\text{Bi}_{0.85}\square_{0.15-y}Me_y[\text{V}_{0.55}\text{Mo}_{0.45-y}\text{Fe}_y]\text{O}_4$. Reaction temperature: 673 K. Pulse composition: 5 μmol of 1-butene. (●) Total conversion, (□) butadiene, (△) 2-butenes, and (○) ($CO + CO_2$)/4.

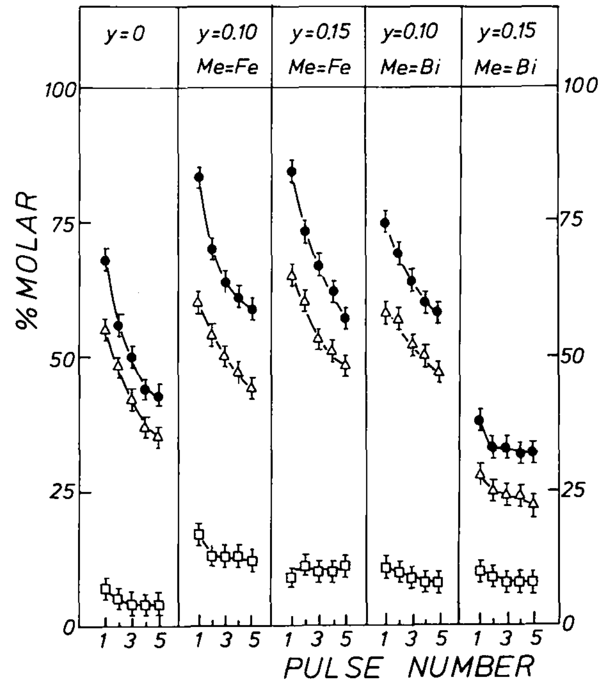

FIG. 4. Oxidative dehydrogenation of 1-butene on $\text{Bi}_{0.85}\square_{0.15-y}Me_y[\text{V}_{0.55}\text{Mo}_{0.45-y}\text{Fe}_y]\text{O}_4$. Reaction temperature: 473 K. Pulse composition and symbols as in Fig. 2.

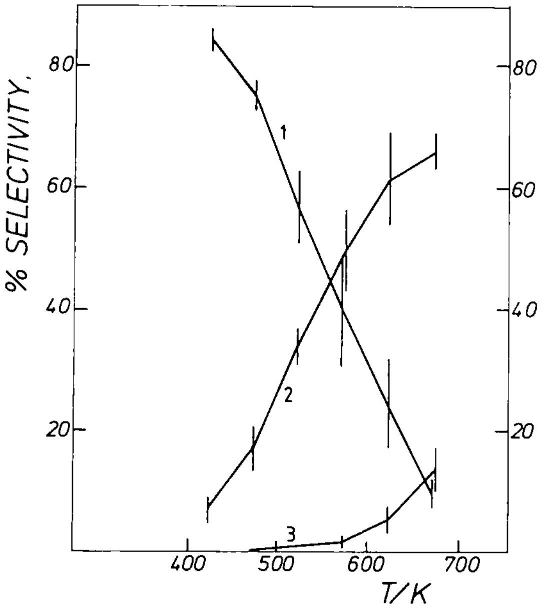

FIG. 5. Dependence of selectivity on reaction temperature. Catalyst $y = 0.10$, Me = Fe. Vertical segments represent the range of values determined in the five pulses of 1-butene. Curve 1, selectivity to 2-butenes; curve 2, selectivity to butadiene; curve 3, selectivity to carbon oxides.

the samples $y = 0$ and $y = 0.15$ Me = Bi. The butadiene yield decreases with catalyst reduction on the samples $y = 0$, $y = 0.10$ with Me = Bi, and $y = 0.15$ with Me = Bi, whereas it increases on the more active catalysts ($y = 0.10$ with Me = Fe and $y = 0.15$ with Me = Fe). The different behavior, however, can be accounted for if one looks at the production of carbon oxides, which is relatively much higher on the latter catalysts, especially in the early pulses. Indeed, the removal of the most reactive oxygen of the catalysts by successive reducing pulses decreases the rate of the accompanying complete oxidation (either direct or consecutive), with the consequence of increasing the amount of butadiene.

At 573 and 473 K (Figs. 3 and 4, respectively) all the catalysts show a significant decrease in total conversion with pulse number. At 573 K the yield of butadiene decreases on all the samples, while the yield of 2-butene isomers increases on the more active catalysts and decreases on the less active ones. At 473 K the picture is clearer (see Fig. 4). The activity (as total conversion) decrease with pulse number is almost completely due to the decrease in the isomerization, the butadiene yield being nearly constant on each catalyst. It is recalled that, especially at low temperature, the reduction of the catalyst by the pulses of hydrocarbon is accompanied also by surface contamination due to small amounts of carbon-containing species.

In order to give a quantitative account of the catalyst reduction, Fig. 6 reports the lattice oxygen lost, O_L (μmol g^{-1}), during the five pulses of 1-butene at the reaction temperatures 673, 573, and 473 K. For a better evaluation of the extent of reduction with the catalyst composition, the amount (μmol g^{-1}) of the oxygen contained in a monolayer is also reported as a dotted line for each catalyst. A surface O^{2-} density of 1.3×10^{19} m^{-2} (corresponding to 21.6 μmol of anions m^{-2}) is assumed. This value is derived for the (1 0 0) plane with the lattice parameters $a = b = 0.52$ nm and $c = 1.17$ nm and does not substantially change if other planes are considered.

The overall picture of the results of Figs. 2–6 indicates that a fast oxygen ion diffusion must take place at high temperature (673 K) so that the oxidation degree of the outermost layer, necessary for the catalytic activity, is rapidly restored in the time scale of the experiment. Nevertheless, the catalyst $y = 0.15$ with Me = Bi seems to be the one for which the oxygen diffusion is comparatively slow, as indicated by the faster decay of the activity with the pulse number, that is, with the catalyst reduction.

Kinetic Parameters

All data reported so far refer to 1 g of sample. A correct comparison, however, of the catalytic activities and of the extents of reduction should obviously take into account the different surface areas of the catalysts. To this end, in Table 2 the specific rate constant for the overall reaction and the catalyst oxygen consumption per unit surface area are shown together with the apparent activa-

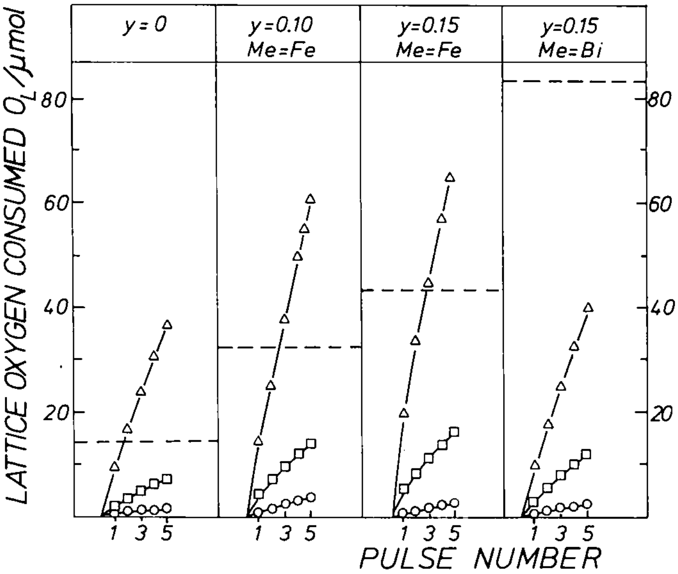

FIG. 6. Lattice oxygen consumed, O_L (μmol/g$_{cat}$), with the pulses of 1-butene. Reaction temperature: (○) 473 K, (□) 573 K, (△) 673 K. Dotted lines indicate the content of oxygen in the monolayer for the various catalysts (see text).

TABLE 2

Specific First-Order Rate Constants of the Overall Reaction, k_{sp}, Catalyst Oxygen Consumption per Unit Surface Area, $O_{L_{sp}}$, and Apparent Activation Energies for the Catalyst Reduction, $E_{a_{red}}$

Catalyst	Temp. (K)	k_{sp}[a] ($m^{-2}s^{-1}$)	$O_{L,sp}$[b] (μmol m^{-2})	$E_{a_{red}}$[c] (kJ mol^{-1})
$y = 0$	673	2.22–1.86	52.2	43
	573	1.46–0.77	10.3	
	473	1.11–0.56	2.0	
$y = 0.10$, *Me* = Fe	673	(1.8)–(1.6)	40.5	36
	623		18.1	
	573	(1.2)–0.61	9.5	
	523		4.5	
	473	0.82–0.41	2.7	
	423		0.7	
$y = 0.15$, *Me* = Fe	673	(1.5)–(1.4)	34.3	40
	573	(0.9)–0.50	8.2	
	473	0.63–0.29	1.6	
$y = 0.10$, *Me* = Bi	673	(3.1)–(2.5)	43.6	32
	573	1.88–1.05	14.7	
	473	1.18–0.74	3.7	
$y = 0.15$, *Me* = Bi	673	0.40–0.28	10.4	38
	573	0.18–0.12	3.2	
	473	0.09–0.07	0.6	

[a] Values for the first and the last pulse of 1-butene. Values calculated from total conversions exceeding 90% are shown in parentheses.

[b] Cumulative values for the five pulses of 1-butene; theoretical oxygen in a monolayer [(100) plane)] = 21.6 μmol m^{-2}.

[c] Apparent activation energy for the catalyst reduction determined in the range 473–673 K.

tion energy for the reduction. The specific rate constant, k_{sp}, was calculated assuming a first-order reaction with respect to 1-butene in a way identical to that employed for the propene oxidation on the same catalysts (2) by means of the equation

$$k_{sp} = [F/(V_{cat} \cdot A)] \cdot \ln[1/(1 - X)], \qquad [5]$$

where F is the flow rate of reactant, which in the present case is approximately equal to the flow rate of carrier gas (cm^3_{STP} s^{-1}), V_{cat} is the catalyst volume (cm^3), A is the exposed area of the sample (m^2), and X is the fractional total conversion of 1-butene. This expression, which holds for a steady-state flow reactor, is formally analogous to that derived by Bassett and Habgood (22) for a first-order reaction in a pulse reactor and can be used for comparative purposes. Due to the high values of the total conversion even at the lower temperature, the error in the evaluation of k_{sp} may well be large, but the data are believed to be reliable for a comparison.

Table 2 again shows that catalyst $y = 0.15$ with *Me* = Bi (no cation vacancies, all eight-coordinated sites being filled by Bi^{3+} ions) has the lowest activity. This result agrees well with that obtained in the propene oxidation (2). Moreover, the lattice oxygen consumption per unit area is comparatively low for $y = 0.15$ with *Me* = Bi (it does not exceed 0.5 monolayer). A systematic variation in the apparent activation energies for the reduction was not found. Indeed, a value of 38 ± 6 kJ mol^{-1} embraces all the reported data.

1-Butene Isomerization

Further insight into the catalytic behavior of the catalysts can be gained from Table 3. A first point, which was also apparent in Figs. 2–5, is that at a given temperature the ratio of butadiene to 2-butenes is significantly higher on all the iron-containing catalysts (irrespective of whether Fe^{3+} is present only in tetrahedral or in both tetrahedral and eight-coordinated sites of scheelite). This result is in agreement with that reported by Linn and Sleight (18), who found higher oxidation to isomerization ratios over $Bi_3FeMo_2O_{12}$ than over $Bi_2Mo_3O_{12}$ for the present reaction in the range 623–723 K. A second point is that the *trans*-2-butene to *cis*-2-butene ratio is near unity, although it tends to decrease either with decreasing temperature or with increasing number of 1-butene pulses. Table 3 also shows that the extent of the isomeri-

TABLE 3

Butadiene to 2-Butenes Ratio, *trans*- to *cis*-2-Butene Ratio, and Extent of Isomerization

Catalyst	Temp. (K)	Butadiene/ 2-butenes[a]	*trans*/ *cis*[a,b]	Isomerization extent[a,c]
$y = 0$	673	2.4–1.9	1.3–1.2	0.26–0.18
	573	0.7–0.5	1.2–1.0	0.12–0.02
	473	0.1–0.1	1.1–0.8	0.04–0.01
$y = 0.10$, Me = Fe	673	8.4–5.7	1.5–1.5	0.79–0.90
	573	1.8–0.9	1.4–1.0	0.46–0.08
	473	0.3–0.3	1.3–0.8	0.18–0.02
$y = 0.15$, Me = Fe	673	8.5–9.7	1.6–1.6	1–1
	573	1.7–1.0	1.5–1.0	0.66–0.10
	473	0.2–0.2	1.4–0.9	0.24–0.02
$y = 0.10$, Me = Bi	673	7.9–4.7	1.4–1.3	0.77–0.49
	573	1.5–0.8	1.3–1.0	0.29–0.06
	473	0.2–0.2	1.1–1.0	0.08–0.02
$y = 0.15$, Me = Bi	673	8.3–7.2	1.2–1.0	0.04–0.01
	573	2.1–1.9	1.0–0.9	0.01–<0.01
	473	0.4–0.3	0.9–0.8	<0.01–<0.01

[a] Experimental values for the first and the last pulse of 1-butene.

[b] The equilibrium values for the *trans*-to-*cis* ratio are 1.55 (at 673 K), 1.66 (at 573 K), and 1.89 at (473 K). Calculated from ΔG_f° in Ref. (23).

[c] The isomerization extent is defined as $[(trans\text{-2-butene} \times cis\text{-2-butene})/(\text{1-butene})^2]/K_1$, where the values of the equilibrium constant $K_1 = [(trans\text{-2-butene} \times cis\text{-2-butene})/(\text{1-butene})^2]_{eq}$ are 3.80 (at 623 K), 7.14 (at 523 K), and 16.60 (at 423 K). Calculated from ΔG_f° in ref. (23)

zation is comparatively high on the catalyst $y = 0.15$ with Me = Fe and very low even at high temperature on the catalyst $y = 0.15$ with Me = Bi. Thermodynamic data for the calculation of the equilibrium constants for the isomerization have been drawn from Ref. (23), assuming ideal behavior.

Reoxidation Behavior

The experimental data of the oxygen recovered by the prereduced catalysts (always with one pulse of 5 μmol of 1-butene at 673 K) as a function of the oxygen pulse number were collected for each sample at three temperatures (473, 573, and 673 K). As an example, the behavior of the catalyst $y = 0$ is shown in Fig. 7. The oxygen uptake is initially comparatively fast, but then the reoxidation rate declines so much, especially at low temperature, that it is virtually impossible to restore the level prevailing before reduction without increasing the temperature to 723 K. This behavior suggests that at least two processes are taking place, namely a surface reoxidation and a diffusion of oxygen ions from the surface into the bulk of the solid. In fact, even if the amount of oxygen lost in the prereduction is less than that contained in a monolayer, the reduction most probably tends to redistribute into the bulk depending on catalyst composition and temperature. Nevertheless, in the initial part of the

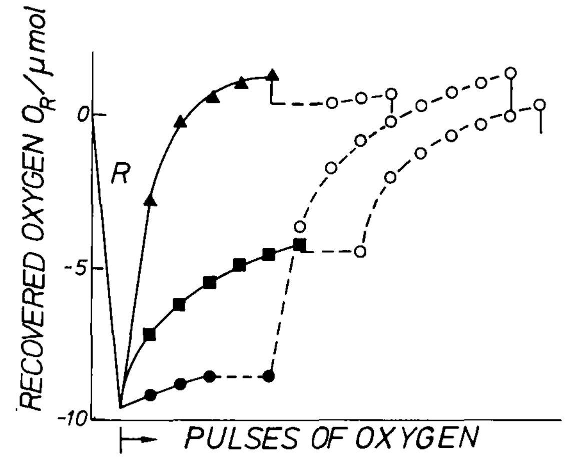

FIG. 7. Oxygen recovered, O_R (μmol/g_{cat}), with pulses of O_2 (5 μmol per pulse). Catalyst $y = 0$ prereduced with a pulse of 1-butene (5 μmol) at 673 K (curve R), before each reoxidation experiment. The value 0 arbitrarily represents the oxidation state of the catalyst after overnight pretreatment with oxygen at 723 K followed by 30 min equilibration with He. Reoxidation temperature: (●) 473 K, (■) 573 K, (▲) 673 K, and (○) 723 K. The amounts of oxygen consumed to convert carbonaceous deposits to CO_2 are also indicated (vertical segments at the end of the reoxidation curves). This amount was estimated assuming that the carbon deposit has the composition of adsorbed butadiene.

TABLE 4

Reoxidation Behavior of the Catalysts Prereduced with One Pulse of 1-Butene at 673 K

Catalyst	$O_{L_{sp}}$[a] (μmol m^{-2})	$k_{ox_{sp}}$[b] (pulse^{-1} m^{-2}) At 673 K	At 573 K	At 473 K	$E_{a_{ox}}$[c] (kJ mol^{-1})
$y = 0$	13.4	0.94	0.20	0.057	36
$y = 0.10$, Me = Fe	7.7	0.20	0.051	0.017	32
$y = 0.15$, Me = Fe	9.5	0.15	0.037	0.015	30
$y = 0.15$, Me = Bi	2.2	0.066	0.039	0.018	17

[a] Lattice oxygen lost in the prereduction.

[b] Apparent first-order kinetic constant for the reoxidation.

[c] Apparent activation energy for the catalyst reoxidation determined in the range 473–673 K.

reoxidation curve first-order kinetics with respect to the oxygen defect can be applied according to the rate equation

$$r_{ox} = \Delta O_{R_i} = k_{ox}\,(O_L^0 - O_{R_i}), \qquad [6]$$

where ΔO_{R_i} is the amount of oxygen recovered by the catalyst during the ith pulse (μmol pulse^{-1}), k_{ox} is an apparent first-order kinetic constant (pulse^{-1}) which also includes a term due to the pressure of O_2 in the pulse (constant in all the experiments), O_L^0 is the lattice oxygen (μmol) lost during the prereduction, and O_{R_i} is the amount of oxygen recovered by the catalyst after i pulses (μmol). The above equation is formally analogous to that reported by Brazdil *et al.* (24).

Table 4 shows the apparent kinetic constants per unit surface area, $k_{ox_{sp}}$, and the apparent activation energies, $E_{a_{ox}}$, for the reoxidation on the studied catalysts. Faster reoxidation occurs, at any temperature, on the catalyst without iron, i.e., $y = 0$, while the sample with all the cationic vacancies filled by Bi^{3+} ions, $y = 0.15$ with Me = Bi, is reoxidized with great difficulty. The apparent activation energies for the reoxidation are very similar, with the exception of the catalyst $y = 0.15$ with Me = Bi, for which a lower value has been determined.

DISCUSSION

The mechanism of allylic oxidation of olefins is rather well established, although there is still controversy concerning the centers involved in the various reaction steps (6–8, 25–29). Concerning the first step (α-hydrogen abstraction and allyl formation), it can in principle be common to the oxidation and isomerization reaction. In this situation, however, the possibility of an allyl carbanion as intermediate is ruled out because a *cis/trans* ratio much higher than 1 would be expected in this case (30, 31). On the contrary, π-allyl radicals can be common intermediates for the two reactions since the actually observed *cis/trans* ratio $\simeq 1$ is that foreseen if radical species were involved (30, 31). A value close to 1 for the above ratio is, however, compatible also with the isomerization mechanism *via* carbenium ions, which can be formed by proton addition to 1-butene at a Brønsted acidic site. Indeed, Forzatti *et al.* (32) found a correlation between low-temperature isomerization and high-temperature total oxidation of 1-butene on molybdenum oxide-based catalysts, attributed to the transformation of Brønsted to Lewis acidic sites with increasing temperature.

Attention is now focused on the oxidative process. Under Results, we showed that the activity trends for butene oxidation are similar to those for the propene oxidation previously studied (2), supporting the view of a common first rate-determining step for both reactions. Moreover, we found that the overall activity, per m^2 of catalytic surface, is significantly lower for the catalyst $y = 0.15$ with Me = Bi, i.e., when the cationic vacancies are completely filled by Bi^{3+} ions. This finding agrees with the results of Sleight (6) and can be understood by considering that the presence of cationic vacancies increases the basicity and the coordinative unsaturation of the surface O^{2-}, making the first hydrogen abstraction easier. However, the main difference between the propene and the butene reaction arises from subsequent steps. In both cases there is a second hydrogen abstraction, but in the propene reaction this abstraction is accompanied by an oxygen insertion to give an adsorbed unsaturated aldehyde, while in the butene reaction the oxygen insertion does not occur, probably due to the considerable stabilization offered by the presence of two conjugated double bonds in the butadiene produced.

Our study has shown that the catalyst $y = 0.15$ with Me = Bi (all vacancies being filled by Bi^{3+} ions), which was very poor in producing acrolein from propene, is rather active in butadiene production. This result points to the importance of the cationic vacancies, in a scheelite catalyst, in the step of oxygen insertion. Indeed, a surface cation vacancy generates, around itself, surface oxygen ions with a higher bond order to the metal cations, and it has been suggested that oxygen ions of this type are those suitable for selective insertion into the allyl intermediate, when the second hydrogen is lost (33). Thus we suggest that the presence of surface cation defects has a double positive effect in the propene oxidation, while in the oxidative dehydrogenation of butene the role of the cationic vacancies would be confined to the first step, i.e., α-hydrogen abstraction and allyl formation.

As shown under Results, a feature of the iron-containing catalysts is that they display higher oxidation to isomerization ratios than the catalyst without iron ($y = 0$). This finding indicates that the presence of a reducible ion, such as Fe^{3+}, increases the rate of oxidation at the expense of that of the isomerization reaction. The hypothesis of a participation of iron ions in the step of butadiene formation is supported by fact that the oxidative dehydrogenation of butene to butadiene proceeds selectively on pure Fe_2O_3 and on iron-containing spinels (20, 34–38).

The behavior of the catalysts toward reoxidation deserves some final comments. The results show that the catalyst with the higher concentration of cation defects ($y = 0$) has the higher reoxidation rate, while the catalysts without cationic vacancies (especially $y = 0.15$ with Me = Bi) have a lower reoxidation rate. This picture is indicative of a different mobility of the lattice oxygen among catalysts. The mobility is higher for the catalyst with the higher concentration of cationic vacancies and lower for the specimens without cationic vacancies. The improvement of lattice oxygen diffusion due to the presence of cationic vacancies in scheelite catalysts has already been pointed out by Brazdil *et al.* (33). On the other hand, two catalysts without cationic vacancies, namely, $y = 0.15$ with Me = Fe and $y = 0.15$ with Me = Bi, show different mobilities of their lattice anions, the latter catalyst showing the lower mobility. Hence, it appears that a correlation between mobility of oxygen ions and number of cationic vacancies is an indirect one, and as suggested by Ueda *et al.* (39), the number of cationic defects is not the only parameter to be considered.

CONCLUSIONS

The results of the present study can be summarized as follows: (i) the first step in the allylic oxidation on our scheelite catalysts is facilitated by the presence of cationic vacancies; (ii) the subsequent step is also facilitated by the cation defects when oxygen insertion occurs, such a role being otherwise absent; (iii) cation defects also have a positive effect by improving lattice oxygen diffusion; and (iv) iron, when present, is involved in the succeeding step by increasing the rate of dehydrogenation of the allyl intermediate at the expense of the isomerization.

ACKNOWLEDGMENT

The authors are grateful to Professor F. S. Stone for reading and commenting on the preliminary manuscript.

REFERENCES

1. Porta, P., Lo Jacono, M., Valigi, M., Minelli, G., Anichini, A., De Rossi, S., and Gazzoli, D., *J. Catal.* **100,** 86 (1986).
2. De Rossi, S., Lo Jacono, M., Porta, P., Valigi, M., Gazzoli, D., Minelli, G., and Anichini, A., *J. Catal.* **100,** 95 (1986).
3. Cordischi, D., Lo Jacono, M., Minelli, G., and Porta, P., *J. Catal.* **102,** 1 (1986).
4. Valigi, M., De Rossi, S., Gazzoli, D., and Porta, P., *Gazz. Chim. Ital.* **116,** 97 (1986).
5. Gazzoli, D., Anichini, A., De Rossi, S., Inversi, M., Lo Jacono, M., Porta, P., and Valigi, M., *J. Catal.* **119,** 277 (1989).
6. Sleight, A. W., *in* "Advanced Materials in Catalysis" (J. J. Burton and R. L. Garten, Eds.), p. 181. Academic Press, New York, 1977.
7. Haber, J., and Grzybowska, B., *J. Catal.* **28,** 489 (1973).
8. Grzybowska, B., Haber, J., and Janas, J., *J. Catal.* **49,** 150 (1977).
9. Hucknall, D. J., "Selective Oxidation of Hydrocarbons." Academic Press, New York, 1974.
10. van der Wiele, K., and van den Berg, P. J., *in* "Comprehensive Chemical Kinetics" (C. H. Bamford and C. F. H. Tipper, Eds.), Vol. 20, p. 123, Elsevier, Amsterdam, 1978.
11. Higgins, R., and Hayden, P., *in* "Catalysis, Specialist Periodical Reports" (C. Kemball, Ed.), Vol. 1, p. 168. Chemical Society, London, 1978.
12. Dadyburjor, D. B., Jewur, S. S., and Ruckenstein, E., *Catal. Rev.-Sci. Eng.* **19,** 293 (1979).
13. Adams, C. R., Voge, H. H. Morgan, C. Z., and Armstrong, W. E., *J. Catal.* **3,** 379 (1964).
14. Keitzer, K., Batist, Ph. A., and Schuit, G. C. A., *J. Catal.* **15,** 256 (1969).
15. Batist, Ph. A., Prette, H. J., and Schuit G. C. A., *J. Catal.* **15,** 267 (1969).
16. Batist, Ph. A., van der Heijden, P. C. M., and Schuit, G. C. A., *J. Catal.* **22,** 411 (1971).
17. Batist, Ph. A., van de Moesdijk, C. G. M., Matsuura, I., and Schuit, G. C. A., *J. Catal.* **20,** 40 (1971).
18. Linn, W. J., and Sleight, A. W., *J. Catal.* **41,** 134 (1976).
19. Centi, G., and Trifirò, F., *Appl. Catal.* **12,** 1 (1984).
20. Kung, H. H., and Kung, M. C., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 33, p. 159. Academic Press, New York, 1985.
21. Mars, P., and van Krevelen, D. W., *Chem. Eng. Sci. Suppl.* **3,** 41 (1954).
22. Bassett, D. W., and Habgood, H. W., *J. Phys. Chem.* **64,** 769 (1960).
23. Stull, D. R., Westrum, E. F., and Sinke, G. C., "The Chemical Thermodynamics of Organic Compounds." Wiley, New York, 1969.
24. Brazdil, J. F., Suresh, D. D., and Grasselli, R. K., *J. Catal.* **66,** 347 (1980).

25. Grasselli, R. K., and Burrington, J. D., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 30, p. 133. Academic Press, New York, 1981.
26. Grasselli, R. K., Burrington, J. D., and Brazdil, J. F., *Faraday Discuss. Chem. Soc.* **72,** 203 (1982).
27. Matsuura, I., *J. Catal.* **33,** 420 (1974); **35,** 452 (1974).
28. Matsuura, I., and Schuit, G. C. A., *J. Catal.* **25,** 314 (1972).
29. Haber, J., *Pure Appl. Chem.* **50,** 923 (1978).
30. Tanaka, K., and Okuhara, T., *J. Catal.* **65,** 1 (1980), and references therein.
31. Tanaka, K., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 33, p. 124. Academic Press, New York, 1985.
32. Forzatti, P., Trifirò, F., and Villa, P. L., *J. Catal.* **52,** 389 (1978).
33. Brazdil, J. F., Glaeser, L. C., and Grasselli, R. K., *J. Catal.* **81,** 142 (1983).
34. Sazanova, N. N., Venjaminov, S. A., and Boreskov, G. K., *Kinet. Catal.* **14,** 1027 (1973).
35. Misono, M., Sakata, K., Ueda, F., Nozawa, Y., and Yoneda, Y., *Bull. Chem. Soc. Jpn.* **53,** 648 (1980).
36. Rennard, R. J., and Kehl, W. L., *J. Catal.* **21,** 282 (1971).
37. Gibson, M. A., and Hightower, J. W., *J. Catal.* **41,** 420 (1976); **41,** 431 (1976).
38. Cares, W. R., and Hightower, J. W., *J. Catal.* **23,** 193 (1971).
39. Ueda, F., Asakawa, K., Chen, C. L., Moro-oka, Y., and Ikawa, T., *J. Catal.* **101,** 360 (1986).