ELSEVIER

Catalysis Today 33 (1997) 139–150

CATALYSIS TODAY

Modification of kinetic parameters by action of oxygen spillover in selective oxidation of isobutene to methacrolein

S. Hoornaerts [a], D. VandePutte [a], F.C. Thyrion [a], P. Ruiz [b], B. Delmon [b]

[a] Unité des Procédés, Faculté des Sciences Appliquées, Université Catholique de Louvain, Voie Minckeleers, 1, 1348 Louvain-la-Neuve, Belgium

[b] Unité de Catalyse et Chimie des Matériaux Divisés, Université Catholique de Louvain, Place Croix du Sud 2, boite 17, 1348 Louvain-la-Neuve, Belgium

Abstract

A kinetic study of the oxidation of isobutene to methacrolein was carried out by varying the reaction temperature and the oxygen and isobutene partial pressure. Catalysts were prepared by mechanically mixing, in different propositions, α-Sb_2O_4 and MoO_3, synthesized separately. Pure oxides and their mechanical mixtures were tested under identical experimental reaction conditions. The presence of α-Sb_2O_4 changes the reaction orders and the activation energy of the reaction. The changes in the kinetic parameters are explained by a remote control mechanism via spillover oxygen (RCM).

A new model which incorporates both the mechanism of site creation (via RCM) and the catalytic reaction at the thus created (or controlled) active sites fits well the experimental data. All the parameters of the new model have a precise physical meaning.

Keywords: Oxygen spillover; Selective oxidation; Isobutene; Methacrolein; Remote control mechanism

1. Introduction

The success of the overall research and development work in catalysis is increasingly dependent on an intensive cooperation between the fundamental scientist and the process engineers. The present paper is the result of such a cooperation.

Catalytic cooperation between separate oxide phases catalysts plays an important role in the selective oxidation of hydrocarbons. This is reflected by the fact that, except for the case of silver, all the corresponding industrial catalysts contain two or several phases. The existence of strong synergies when different oxides are mixed together shows that this cooperation is a fundamental phenomenon in selective oxidation [1,2].

The synergetic effects can be explained by a relatively long distance action exerted by one oxide phase on the other. The process involves the activation of a small amount of molecular oxygen on some oxide phases (donors) which form mobile species (spillover oxygen). These species migrate to the other oxide phase (acceptor), react with its surface and in this way create or regenerate the sites necessary to form selectively the partially oxygenated products. This is the remote control mechanism (RCM).

The proof of the existence of a RCM rests on a series of experiments using simple mixtures of

PII S0920-5861(96)00109-5

separately prepared powders of donors with given acceptors. Physico chemical measurements allowed alternative explanations of the synergy such as new phase formation, surface contamination, classical bifunctional mechanisms, etc., to be ruled out.

The RCM operates in a large variety of reactions involving oxygen: the oxidation of olefins to unsaturated aldehydes (e.g. isobutene to methacrolein), the oxidative dehydrogenations of butene to butadiene, propane to propene or ethanol to acetaldehyde, the oxidations of ethanol to acetic acid or butane to maleic anhydride, the dehydration/dehydrogenation of *sec*-butanol to butene and methyl ethyl ketone and the oxygen-aided dehydration of *N*-ethyl formamide to proprionitrile.

On the other hand, studies reported in the literature concerning the kinetics of the oxidation of olefins to unsaturated aldehydes are contradictory. In these studies, different formulations of the catalysts have been studied. Many of them are based on bismuth molybdates or multicomponent catalysts. Analysing these investigations, the following observations might be made: (i) For similar catalysts, different kinetic model have been proposed, (ii) in a same series of measurements, the reaction orders vary in function of the experimental conditions, (iii) this leads the authors to the surprising conclusion that the rate determining step of the reaction is different for similar catalysts [3–8].

It seems thus that new kinetic models are necessary to correlate in a more adequate way experimental data, in particular when several phases are present in the catalysts. The objective of this paper is to emphasise these aspects, proposing a new kinetic model to fit experimental data.

2. Basis for a new kinetic model based in the RCM

During the selective oxidation of the hydrocarbon, spillover oxygen controls the dynamic surface phenomena of the continuous oxido-reduction process (so called Mars–Van Krevelen process) which explains the catalytic reaction. The oxido-reduction mechanism implies that structures and the coordination of the atoms on the catalyst surface continuously change during catalysis. The central idea of our proposal is that a side mechanism, involving spillover oxygen, avoids too large fluctuations in surface coordination during the catalytic reaction. This results in a steady-state situation in which selective sites are continuously restored by the effect of O_{so} on the acceptor but continuously, slowly deactivated because of the occurrence of the catalytic reaction or, more precisely, of a harmful side-reaction occurring in parallel with the main one. The kinetic model must therefore take into account this action of spillover oxygen.

The models based on the Mars–Van Krevelen picture do reflect the local oxido-reduction process, but they generally fail to reflect the changes of selectivity observed when the surface gets more or less reduced, as a function of the reaction conditions. They also completely neglect the influence of the donor phase and the spillover oxygen it emits.

The new kinetic model is based in the classical Mars–Van Krevelen model, but it incorporates both the mechanism of site creation (via RMC) and the catalytic reaction at the thus created (or controlled) active site.

Details of the development of the new kinetic model has been given elsewhere [9]. The kinetic equation represents adequately the isothermal experimental data obtained during the oxidation of isobutene to methacrolein on mechanical mixtures of various compositions of an acceptor and a donor prepared separately [9]. The model is based essentially on the fact that, when the remote control operates, the fraction (called ρ') of the acceptor surface which permits the reduction–oxidation process of the selective catalytic reaction (called surface S') depends on (i) the relative amount of donor added to the acceptor characterized by a mass ratio R_m, (ii) the oxygen pressure (p_o) which, through the dissociation to O_{so}, modifies the concentration of O_{so} on the acceptor surface, (iii) the pressure of the isobutene (hydrocarbon), p_{C4} and (iv) the temperature. The new model incorporates, in two different terms, both the mechanism of site creation (by the RMC relation ρ') and the catalytic reaction at the thus created active site (Reaction Kinetics):

$$\text{rate} = F_{rc}(R_m, p_o, p_{C4}, T) \times (\text{Reaction Kinetics})$$

In this study, we have considered that the reaction kinetics on each of these created sites is given (for example) by a Mars–Van Krevelen kinetic equation. In principle, other models representing adequately the reaction kinetic mechanism on the acceptor can also be considered. Per unit surface area of the selective surface S', on which the selective-reduction oxidation process occurs, the rate of reduction (r'_{red}) by isobutene and the rate of oxidation (r'_{ox}) by O_2 are equal, at the steady state, to the rate (per unit of S') of the catalytic reaction on the acceptor (r'), namely $r' = r_{red} = r_{ox}$. Two different kinetics are considered: (i) Kinetics 1: the rate of oxidation is limited by the rate of adsorption of molecular oxygen ($r'_{ox} = k_{ox}\, p_o \alpha'_{red}$), and (ii) Kinetics 2: the rate of oxidation is limited by the dissociation of molecular oxygen ($r'_{ox} = k_s\, p_{ox}^{1/2} \alpha'_{red}$), where k_{ox} and α'_{red} are the oxidation rate constant and the fraction of reduced surface S'.

The total rate (r_{ta}) for a given amount of catalyst of a given composition R_m where the total acceptor surface area is S (namely $S' = S\rho'$), is given by:

$$r_{ta} = S\rho' \frac{k_{red}\, p_{C4} k_{ox}\, p_o}{k_{red}\, p_{C4} + k_{ox}\, p_o}$$

× (if oxidation is limited by adsorption, Kinetics 1)

$$r_{ta} = S\rho' \frac{k_{red}\, p_{C4} k_{ox}\, p_o^{0.5}}{k_{red}\, p_{C4} + k_{ox}\, p_o^{0.5}}$$

× (if oxidation is limited by dissociation, Kinetics 2)

where ρ' is given by the 'remote control' relation as explained above.

The rate r_a per unit surface area of the acceptor contained in the mixture is given respectively by:

$$r_a = \rho' \frac{k_{red}\, p_{C4} k_{ox}\, p_o}{k_{red}\, p_{C4} + k_{ox}\, p_o} \text{ (Kinetics 1)} \qquad (1)$$

$$r_a = \rho' \frac{k_{red}\, p_{C4} k_{ox}\, p_o^{0.5}}{k_{red}\, p_{C4} + k_{ox}\, p_o^{0.5}} \text{ (Kinetics 2)} \qquad (2)$$

When the acceptor is alone, the fraction of the surface permitting the selective reduction–oxidation process is not influenced by the remote control effect. Then k_{red} and k_{ox} could, in principle, be obtained separately from adequate experiments such as thermoreduction, thermoxidation, TAP, etc. In this study relative values of k_{red} and k_{ox} were obtained from the variations of r_a as a function of p_{C4} and p_o for single oxide catalyst. The parameter ρ' then takes the value ρ'_1 corresponding to the fraction of the surface which is spontaneously selective in single oxide catalyst. The results with R_m different from 1.0 will thus correspond to ratios of the corresponding ρ' to ρ'_1 (namely ρ'/ρ'_1). These values can be calculated from r_a, by fitting the experimental data obtained with the acceptor–donor mixtures.

The model which considers that the rate of oxidation is limited by the dissociation of molecular oxygen [Eq. (2)] had been tested in the selective oxidation of isobutene to methacrolein on catalysts made of mechanical mixtures of α-Sb_2O_4 + MoO_3 [9]. The changes of ρ'/ρ'_1 with the amount of α-Sb_2O_4 were well correlated with the experimental data. This proved, in agreement with the RCM, that the fraction of the surface of single oxide catalyst which carried out selectively the oxidation via the oxido-reduction process depended of the degree of irrigation of MoO_3 by spillover oxygen produced on α-Sb_2O_4.

The logical extension of the work was: (i) to verify if the parameter ρ'/ρ'_1 could be always correlated with the RCM using the same kinetic equation [Eq. (2)], but at different temperatures and (ii) to investigate if the parameter could be correlated with the RCM using a model in which the rate of oxidation is limited by the adsorption of molecular oxygen [Eq. (1)], and this at all temperatures and (iii) to compare the fitting of the experimental results using this last model and the classical Mars–Van Krevelen model.

We would like to emphasize that our objective is not to discriminate between the different mechanisms involved in the reaction ['Reaction Kinetics' term in Eq. (1)], but to show that the model incorporating two different terms can also fit correctly the experimental results when the reaction kinetics are either Kinetics 1 or Kinetics 2. Selection of the better of these two models is out of the scope of the present study.

In order to show the advantage of the form proposed for the kinetic equation, we have also calculated the empirical order of reaction on the basis of equations:

$$r_a = kp_{C4}^n \text{ and } r_a = kp_o^m \tag{3}$$

As a first approximation, the empirical activation energies were calculated by plotting the logarithm of the reaction rate as function of the inverse of the temperature. For that, the following rate equation has been used:

$$r_a = k_o(\exp - (E/RT))p_{C4}p_o \tag{4}$$

The donor α-Sb_2O_4 is completely inert in the oxidation of isobutene to methacrolein. No decomposition of isobutene or reaction products were observed when pure α-Sb_2O_4 was used as catalyst. (This justifies the assumption that the synergy observed and the changes in the kinetic parameters are due to a RMC, namely that the single role of α-Sb_2O_4 is to control the catalytic activity of MoO_3.)

The conversion was always maintained at a low value, normally at about 10% and not higher than 15%, by varying the contact time. This was done by changing the amount of catalyst. Reaction rate was measured for pure oxides and their mechanical mixtures at different partial pressures of isobutene and partial pressures of oxygen, and at different reaction temperatures.

3. Experimental

3.1. Preparation of the catalyst oxides

α-Sb_2O_4 was prepared by calcination of Sb_2O_3 (p.a. UCB) in air at 500°C for 20 h. MoO_3 was obtained by thermal decomposition of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (p.a. Merck) in air at 500°C for 20 h. BET surface area of both oxides were about 1 m^2/g.

3.2. Mechanical mixtures of acceptor and donor

The mechanical mixtures, which we shall also call biphasic catalysts, were prepared by dispersing adequate amounts of both powders in 200 ml of *n*-pentane. The suspension was agitated vigorously with an Ultra-turrax equipment at 6000 *t*/min during 10 min and subsequently ultrasonically for 3 min. The *n*-pentane was evaporated under reduced pressure, while continuing the agitation at 25°C. The solid was dried in air at 100°C overnight. The corresponding mechanical mixtures were subjected to no further calcination. The mixture was pressed into wafers, then gently broken. Fraction between 315 and 500 μm was used. The granulometry of the catalyst is thus not too small, and permits easy flow of the reacting gas. The pure oxides were treated exactly in the same way as the mixtures. The composition of the mixtures was expressed as the mass ratio:

$$R_m = \frac{\text{weight of } MoO_3}{\text{weight of } MoO_3 + \text{weight of } \alpha - Sb_2O_4}$$

Mechanical mixtures with $R_m = 0.0$ (pure α-Sb_2O_4); 0.25; 0.5; 0.75 and 1.0 (pure MoO_3) were prepared.

3.3. Catalytic test

3.3.1. Test equipment and general test conditions

Catalytic measurements were performed in a conventional fixed-bed reactor system at atmospheric pressure. The reactor was made of a Pyrex U-tube of 8 mm internal diameter into which the catalyst was packed. The amount of catalyst was varied from experiment to experiment in order to have conversions in the range 5 to 15% (amount of catalysts between 300–1600 mg). The catalytic bed was deposited over a small glass bed (spheres of diameter 1 mm) of a height of 10 cm and under another bed 3 cm high. Catalytic tests were realized at atmospheric pressure. The reactant mixture contained isobutene and oxygen diluted with helium. The total feed rate was 45 ml/min in all cases. Reactants were preheated in the furnace used for housing the reactor and were introduced at the bottom of the reactor. The exit gas containing the non-reacted reactants and the products (methacrolein, CO_2 and water) was maintained at 150°C to avoid any condensation. Reactants and products were analysed by gas chromatography. The chromatograph (Intersmat IGC 121 ML) was connected to an integrator (Intersmat ICR-1B). It was equipped with a catharometer, and two columns (1/8″) were used: a Porapak Q (2.5 m length) to analyse isobutene, water and CO_2 and a Tenax (2.5 m length) to analyse methacrolein and acrolein.

Methacrolein was the main selective product (about 95% of the selective oxidation products). Traces of acrolein were detected. No other partial oxygenated product was observed. The carbon mass balance has been calculated in all experiments and was always better than 90%.

3.3.2. Diffusional limitations into the pores of the catalysts

In order to detect the possible intervention of diffusional phenomena, preliminary tests were realized with three fractions of different granulometry: 100–315, 315–500 and 500–800 μm. The standard reaction conditions were as follows: partial pressure of isobutene 10.1 kPa, partial pressure of oxygen 20.3 kPa, total pressure 101 kPa, (including helium). The reaction temperature was 380, 400, 420, 440 and 460°C. The reaction rates were about the same for all catalyst granulometries, indicating that the intraparticle diffusion had no influence on the rates observed [10].

3.3.3. Standard test varying the partial pressure of oxygen

The procedure for a test was as follows: with a mixture corresponding to a partial pressure of oxygen of 30.4 kPa, a partial pressure of isobutene of 10.1 kPa and the rest helium was used. The total corresponded to atmospheric pressure. The reactor was stabilized to the desired temperature. Analysis of reactants and products were realized during two hours. After that, the gas composition was changed by decreasing the partial pressure of oxygen to 20.3 kPa and maintaining the partial pressure of isobutene constant. The partial pressure of helium was changed to maintain the total pressure at atmospheric pressure. Analysis were realized during two hours and then the partial pressure of oxygen was decreased to a lower value, increasing correspondingly the helium pressure. The same procedure as above was followed for other partial pressures of oxygen: 10; 5.1; 2.5 and 1.0 kPa. The tests were made at 380, 400 and 440°C.

3.3.4. Standard test varying the partial pressure of isobutene

A procedure identical to that indicated in Section 3.3.3 was followed. The partial pressure of oxygen was fixed at 10.1 kPa, the partial pressure of isobutene at 2.5 kPa and the total pressure balanced with helium was atmospheric pressure. After stabilization of the temperature, samples were taken during 2 h. The same procedure was followed with other partial pressures of isobutene. The partial pressure of isobutene was increased at 5.1, 10.1 and at 20.3 kPa,

Table 1
Values of the k_{red} and k_{ox} and activation energy obtained after smoothing the values of the parameter obtained with pure MoO_3 ($\rho'/\rho'_1 = 1$)

	Temperature (°C)	k_{red}	k_{ox}	E_{red} (KJ/mol)	E_{ox} (kJ/mol)
Eq. (1)	380	0.0019	0.010	68.3	45.6
Eq. (1)	400	0.0023	0.013	68.3	45.6
Eq. (1)	440	0.0053	0.021	68.3	45.6
Eq. (2)	380	0.0015	0.017	76.2	159.3
Eq. (2)	400	0.0026	0.040	76.2	159.3
Eq. (2)	440	0.0050	0.200	76.2	159.3

always with an atmospheric total pressure. The reaction temperature was 380, 400 and 440°C.

3.4. Numerical methods

The fitting of the parameters of the theoretical models was based on the 'least square' method. This method provides the set of variable parameters of the chosen model which minimizes the sum of the squares of the differences between the experimental values of the rate (V_{exp}) and those given by the theoretical model (V_{model}). The kinetic parameters of the model reported in this work are those for which the function $F = (\Sigma(V_{model} - V_{exp})^2)/n)$, in which n is the number of experimental points, is smaller than 10^{-1}.

4. Results

4.1. Estimation of k_{red}, k_{ox} and ρ'/ρ'_l parameters

When the models given by Eqs. (1) and (2) were fitted to the experimental data obtained for pure MoO_3, some dispersion in the values of k_{red} and k_{ox} obtained for the different temperatures was observed. Dispersion was higher in the case of Eq. (2). We have therefore smoothed the values of the parameters by imposing that the results at the three measurement temperatures correspond exactly to an Arrhenius plot. The results of the smoothing is given in Table 1. The activation energies obtained correspond to values reported in the literature for oxide catalysts in allylic oxidation [3,4,8].

In Tables 2 and 3, we report the ρ'/ρ'_1 values obtained when fitting the experimental data to the new model [Eq. (1) or Eq. (2)] using the k_{red} and k_{ox} values obtained from the data concerning pure MoO_3 (Table 1).

In both cases, the parameter ρ'/ρ'_1 increases with the amount of α-Sb_2O_4 in the mixtures and with the temperature. The variation with temperature of ρ'/ρ'_1 can be expressed, for convenience, using an Arhenius representation. The

Table 2
Values ρ'/ρ'_1 obtained by fitting the experimental data to Eq. (1). For the mixtures the values of k_{red} and k_{ox} have been taken as identical to those obtained after smoothing the values obtained fitting the model with the experimental data concerning pure MoO_3 ($\rho'/\rho'_1 = 1$, Table 1)

Catalyst	Temperature (°C)	ρ'/ρ'_1	$k_{red}\ 10^3$ (Pa^{-1})	$k_{ox}\ 10^3$ (Pa^{-1})	$F\Sigma$ $(V_{model} - V_{exp})^2$
MoO_3 (75%) + α-Sb_2O_4(25%)	380	0.25	1.9	10.1	4.0×10^{-4}
	400	0.49	2.3	13.0	9.4×10^{-4}
	440	0.96	5.3	20.1	0.034
MoO_3 (50%) + α-Sb_2O_4 (50%)	380	0.43	1.9	10.1	0.008
	400	0.86	2.3	13.0	0.041
	440	2.32	5.3	20.1	0.544
MoO_3 (25%) + α-Sb_2O_4 (75%)	380	0.78	1.9	10.1	0.006
	400	3.37	2.3	13.0	0.057
	440	4.72	5.3	20.1	0.158

Table 3
Values ρ'/ρ'_l obtained by fitting the experimental data to Eq. (2). For the mixtures the values of k_{red} and k_{ox} have been taken as identical to those obtained after smoothing the values obtained fitting the model with the experimental data concerning pure MoO_3 ($\rho'/\rho'_l = 1$, Table 1). In parenthesis, values of k_{red}, k_{ox} and ρ' obtained by fitting the experimental values without setting the values of k_{red} and k_{ox} to those obtained with pure MoO_3 data

Catalyst	Temperature (°C)	ρ'/ρ'_l	$k_{red}\ 10^3$ (Pa^{-1})	$k_{ox}\ 10^3$ (Pa^{-1})
MoO_3 (100%)	380	1.0 (0.013)	1.5 (8.4)	17.0 (12.4)
	400	1.0 (0.008)	2.6 (47.9)	40.0 (41.9)
	440	1.0 (0.009)	5.0 (40.4)	200.1 (46.3)
MoO_3 (75%) + α-Sb_2O_4(25%)	380	0.45 (0.008)	1.5 (5.3))	17.0 (8.9)
	400	0.56 (0.016)	2.6 (4.4)	40.0 (110.8)
	440	0.93 (0.096)	5.0 (3.1)	200.1 (149.2)
MoO_3 (50%) + α-Sb_2O_4 (50%)	380	0.85 (0.012)	1.5 (5.5)	17.0 (9.7)
	400	1.04 (0.061)	2.6 (36.4)	40.0 (3.7)
	440	2.28 (0.126)	5.0 (4.3)	200.1 (96.0)
MoO_3 (25%) + α-Sb_2O_4 (75%)	380	1.41 (0.016)	1.5 (12.0)	17.0 (8.5)
	400	3.78 (0.064)	2.6 (8.4)	40.0 (41.5)
	440	4.53 (0.106)	5.0 (15.8)	200.1 (102.6)

thermal increments expressed as 'apparent activation energies' are, for Eq. (1): 30.4, 38.5 and 38.8 kJ/mol and for Eq. (2): 24.7, 23.4 and 17.0 kJ/mol at R_m equal to 0.75, 0.5 and 0.25, respectively.

In Table 3 we also report for comparison (in parenthesis), the ρ', k_{ox} and k_{red} values obtained when fitting the model without imposing the values obtained with pure MoO_3. An important dispersion in the results is obtained. No correlation is obtained as function of the temperature or the amount of α-Sb_2O_4.

In Table 4 we reported the values of k_{red} and k_{ox} obtained by fitting the experimental data to Eq. (1) considering $\rho'/\rho'_l = 1$, namely the values of the parameters corresponding to the classical Mars–Van Krevelen model. The comparison of the values of the function F in Table 2 with those presented in Table 4, show that the fitting is better in the case of the classical Mars–Van Krevelen model. The values of k_{red} and k_{ox} increase when the temperature increases. However, when the amount of α-Sb_2O_4 in the mixtures increases, k_{red} and k_{ox} are modified. Figs. 1 and 2 presents the Arrhenius plot for the k_{red} and k_{ox} values. Two important observations can be obtained from these figures: (i) for k_{red} a linear correlation can be obtained and the activation energy becomes higher when R_m is higher and (ii) for k_{ox} a significant dis-

Table 4
Values of k_{red} and k_{ox} obtained by fitting the experimental data to Eq. (1) considering $\rho'/\rho'_l = 1$ (namely the classical Mars–Van Krevelen model)

Catalyst	Temperature (°C)	ρ'/ρ'_l	$k_{red}\ 10^3$ (Pa^{-1})	$k_{ox}\ 10^3$ (Pa^{-1})	$F\Sigma$ $(V_{model} - V_{exp})^2$
MoO_3 (75%) + α-Sb_2O_4(25%)	380	1.0	0.3	2.6	7.8×10^{-4}
	400	1.0	1.0	17.4	4.5×10^{-4}
	440	1.0	4.0	149.9	0.003
MoO_3 (50%) + α-Sb_2O_4 (50%)	380	1.0	2.0	1.1	0.005
	400	1.0	2.8	4.6	0.037
	440	1.0	9.8	159.8	0.391
MoO_3 (25%) + α-Sb_2O_4 (75%)	380	1.0	3.5	1.6	3.1×10^{-4}
	400	1.0	9.1	23.8	0.044
	440	1.0	23.0	143.6	0.096

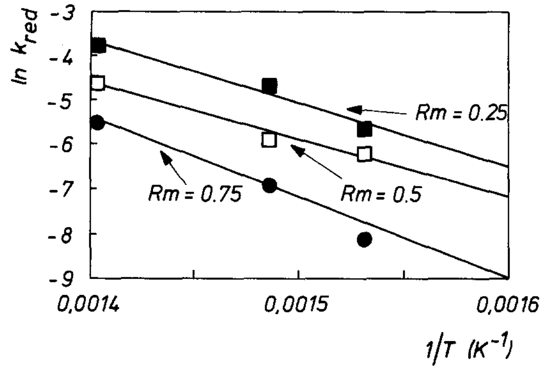

Fig. 1. Arrhenius plot for k_{red} obtained by fitting the experimental data to equation 1 considering $\rho'/\rho'_1 = 1$ (Table 4, parameters corresponding to the classical Mars–Van Krevelen model).

persion is observed and no linear correlation can be obtained for k_{ox} values. This indicates that in spite of a lower values of the F function, the values of k_{red} and k_{ox} have not a precise physical signification.

4.2. Empirical parameters values

As indicated above, we also calculated the values of the reaction orders and the activation energies using empirical formulas [Eqs. (3) and (4)].

Figs. 3 and 4 present typical results showing the variation of the rate of formation of methacrolein as a function of the partial pressure of oxygen, for various mass ratios and temperatures.

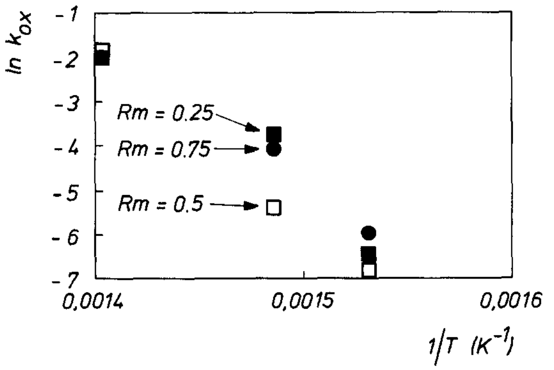

Fig. 2. Arrhenius plot for k_{ox} obtained by fitting the experimental data to equation 1 considering $\rho'/\rho'_1 = 1$ (Table 4, parameters corresponding to the classical Mars–Van Krevelen model).

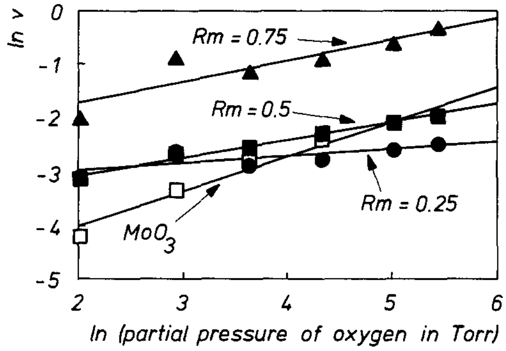

Fig. 3. Dependence of the rate of formation of methacrolein as a function of the partial pressure of oxygen for pure MoO_3 and the mechanical mixtures with $R_m = 0.25$, 0.5 and 0.75 respectively. Temperature of reaction, 400°C.

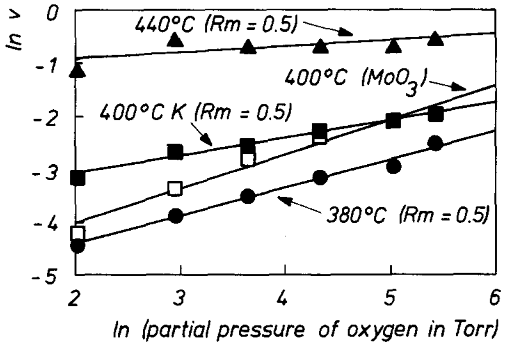

Fig. 4. Dependence of the rate of formation of methacrolein as a function of the partial pressure of oxygen for pure MoO_3 and the mechanical mixtures with $R_m = 0.5$. Temperatures of reaction, 380, 400 and 440°C.

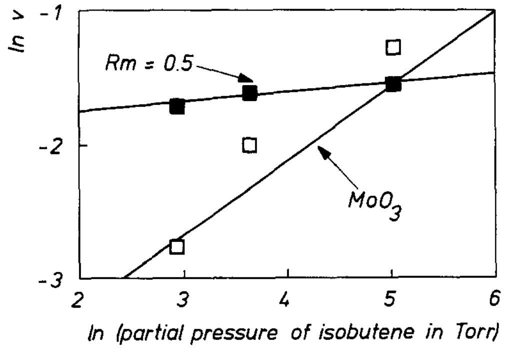

Fig. 5. Dependence of the rate of formation of methacrolein as a function of the partial pressure of isobutene for pure MoO_3 and the mechanical mixtures with $R_m = 0.5$. Temperature of reaction, 400°C.

Table 5
Empirical reaction order [Eq. (3)] for oxygen with pure MoO_3 and mechanical mixtures containing α-Sb_2O_4

Temperature °C	MoO_3 (100%)	MoO_3 (75%)+ α-Sb_2O_4 (25%)	MoO_3 (50%)+ α-Sb_2O_4 (50%)	MoO_3 (25%)+ α-Sb_2O_4 (75%)
380	0.59	0.54	0.51	0.62
400	0.53	0.36	0.33	0.26
440	0.57	0.06	0	0.02

Fig. 5 presents the variation of the formation of methacrolein as a function of the partial pressure of isobutene for various R_m.

Figs. 3–5 indicate that the empirical reaction order depends strongly from the amount of antimony oxide in the mixture and from the temperature. Isobutene and oxygen reaction orders were calculated using Eqs. 3. When comparing orders obtained with pure MoO_3 and those obtained with the mixtures, important differences have been observed.

4.2.1. *Empirical order with respect to the oxygen partial pressure (Table 5)*

(i) For pure MoO_3, the reaction order remains unchanged with the temperature (at a value of about 0.6); (ii) in the mixtures, at 380°C, the order calculated with the mixtures remains unchanged, when the amount of α-Sb_2O_4 increases (about 0.6). When the temperature increases, the order decreases and tends to zero, (iii) when temperature increases, the order decreases more significantly when the α-Sb_2O_4 proportion is higher.

Table 6
Empirical reaction order [Eq. (3)] for isobutene with pure MoO_3 and its mechanical mixtures with α-Sb_2O_4

Temperature °C	MoO_3 (100%)	MoO_3 (50%)+ α-Sb_2O_4 (50%)
380	0.85	−0.05
400	0.75	0.08
440	0.70	0.84

Table 7
Empirical activation energies [Eq. (4)] values for pure MoO_3 and its mechanical mixtures with α-Sb_2O_4

	MoO3 (100%)	MoO_3 (75%)+ α-Sb_2O_4 (25%)	MoO_3 (50%)+ α-Sb_2O_4 (50%)	MoO_3 (25%)+ α-Sb_2O_4 s(75%)
E (kJ/mol)	88.6	139.7	168.0	174.8

4.2.2. *Empirical order with respect to the isobutene partial pressure (Table 6)*

For pure MoO_3, the order varies from about 0.85 to 0.70 when the temperature increases. In the mixture, the order changes: at low temperature (380 and 400°C) it is zero for the catalyst containing 50% of α-Sb_2O_4. The mixture shows similar order as pure MoO_3 for high temperature (440°C).

4.2.3. *Empirical activation energy*

The logarithm of the experimental reaction rate as a function of the inverse of the temperature [Eq. (4)] is a straight line. The empirical activation energy obtained for the catalysts containing pure MoO_3 and various contents of α-Sb_2O_4 are presented in Table 7. The activation energy increases when the content of α-Sb_2O_4 in the catalyst increases.

5. Discussion

It is interesting to explain the trends observed in the alteration of the empirical values as the various parameters change. The first observation is that the kinetic parameters are different when a donor is present, compared to those observed in its absence. The RCM provides the explanation: this is not due to any modification of the kinetics of reduction of the surface by the hydrocarbon or of reoxidation by molecular oxygen. This simply reflects the modification of the area which undergoes the reduction–oxidation process. When MoO_3 is alone, the dependence with respect to the oxygen partial pressure as measured by reaction orders is high because the reoxidation is difficult (Table 5, Figs. 3 and 4). Conversely, the reoxidation at higher temperatures is easier when α-Sb_2O_4 is present, giving a lower order with respect to the partial pressure of oxygen. When the temperature increases, the reoxidation rate of pure MoO_3 increases but simultaneously MoO_3 becomes more active. As a consequence, the empirical order with pure MoO_3 remains high, even at high temperature. In the mixtures, the order is lower at high temperatures because the flow of O_{so} is sufficiently high to allow a good irrigation of O_{so} on MoO_3, permitting in this way a higher reoxidation rate of MoO3, even if it is highly active and hence gets reduced faster.

The variation of the order with respect to isobutene in the catalysts with $R_m = 0.5$ is also logical (Table 6 and Fig. 5). Reduction does not play any rate-limiting role at low temperatures (as it did in pure MoO_3), as indicated by the very low reaction order. This is not the case any more at high temperature, where reoxidation is rapid (Table 6).

The presence of α-Sb_2O_4 changes the apparent energy of activation of the reaction also. Only 25% of α-Sb_2O_4 in the mixtures corresponds to an increase of more than 60% (Table 7). These observations point to the fact that the quantity ρ' results from an activated phenomena, namely the migration of the O_{so} from the α-Sb_2O_4 to the MoO_3.

Results presented in Tables 2 and 4 show that the fitting for the classical Mars–Van Krevelen model with Kinetics 1 is slightly better. However in this case the values of the k_{ox} and k_{red} parameters are quite dispersed (Figs. 1 and 2), and it is not possible to get conclusive information on the influence of the amount of α-Sb_2O_4 in the mixtures on their values. No physical meaning can be directly attributed to these values. This indicates that, when α-Sb_2O_4 is present in the mixtures, another mechanism is involved, that the classical Mars–Van Krevelen model is not able to interpret.

In attempts to fit simultaneously the three parameters of the model [Eq. (2), Table 3], no self-consistent values are obtained. This is understandable, as too many parameters are allowed to vary for a set of data containing too few elements. We remark that similar results have been observed in the case of the fitting of Eq. (1).

On the contrary when the values of k_{ox} and k_{red} corresponding to MoO_3 are imposed, a coherent picture emerges (Tables 2 and 3). As expected, the fraction of the surface active (namely ρ') in the reduction–oxidation mechanisms increases when the proportion of α-Sb_2O_4 in the mixture or when the temperature increase. More precisely, if we accept that the remote control operates, one finds that a clear correlation exists between ρ'/ρ'_1 and the amount of α-Sb_2O_4 and the temperature, when the parameters k_{red} and k_{ox} are set equal to those of pure MoO_3. The comparison of the two ways of expressing the results, namely our modified Mars–Van Krevelen equation and the empirical expression, underline the fact that what is important in the modelling is the separation of the two terms in the kinetic equation, thus confirming our previous results. The fact that the results are qualitatively similar for Kinetics 1 and Kinetics 2 is a confirmation of that. The tendency is exactly the same in both cases. The present results thus provide clues for explaining divergences observed in the literature concerning the reaction order, activation energies of the reaction, limiting step in the mechanism (reduction or reoxidation rate) and overall kinetic model.

Two final comments seem necessary:

First, it can be expected in most cases that the values of ρ'/ρ'_1 be higher than 1 for the mixtures because the fraction of the acceptor surface which permits the reduction–oxidation process of the selective catalytic reaction is expected to be higher in the presence of α-Sb_2O_4, which emits spillover oxygen. But the presence of the donor (α-Sb_2O_4) constitutes only one of the parameters which determine the fraction of the surface which is active in the oxido-reduction mechanism. As discussed above, this value depends of, (i) the relative amount of donor added to the acceptor (R_m), (ii) the oxygen pressure (p_o), (iii) the pressure of the isobutene, p_{C4} and (iv) the temperature. Then, the fraction of the acceptor which is selective is the consequence of a balance of different phenomena which occurs simultaneously: (i) the ability of the donor to produce O_{so}, (ii) the rate of diffusion of O_{so} from the donor to the acceptor, (iii) the rate of reaction between the O_{so} with the acceptor, etc. In general, the coupling of these phenomena lead to an increase in the selectivity and in the yield of the selective products explaining the synergetic effects. Under some particular conditions the increase in the selectivity is favoured preferentially with respect to the yield. But under other conditions, yield and selectivity or only yield may be promoted. The consequence is that in some less favorable conditions, it cannot be excluded that the ρ'/ρ'_1 values be lower than 1. However it is necessary to emphasise that even in these conditions the selectivity of the catalysts would nevertheless be significantly higher compared to those observed in the absence of donor(high synergetic effect on the selectivity). The variation in the synergetic effect or more precisely the increase of the conversion, yield or selectivity due to the presence of the donor of Oso has been discussed extensively previously [1,2].

Second, in this work we have correlated the changes in the number of selective sites with the parameter ρ'/ρ'_1. This has been made in order to emphasises that the presence of α-Sb_2O_4 changes the fraction of the surface of MoO_3 which is selective during the reaction. This fraction depends of the rate of reduction and reoxidation of MoO_3. The principal reason of the increase in the number of selective sites is the increase in the reoxidation rate. The increase in the reoxidation rate has been often cited as one of the reasons explaining the increase in the selectivity. The fact that the k_{ox} values are too dispersed when the parameter $\rho'/\rho'_1 = 1$ (Table 4), or when it is fitted simultaneously with k_{ox} and k_{red} (Table 3) is an indication that the classical Mars–Van Krevelen kinetics is not able to correctly account for the data. A new form of kinetic models is necessary. Our new model represents satisfactorily the relation between the increase in the reoxidation rate and the experimental results because the separate term reflecting the remote control is considered. One could argue that another possibility would be to modify the classical Mars–van Krevelen model in order to take into account the increase of the k_{ox} parameter in a different way. One possibility is to add a 'new term' in the Mars–Van Krevelen model considering that the reoxidation constant parameter varies as $k_{ox} + \Delta k_{ox}$ with Δk_{ox} being the increase of k_{ox} due to the presence of α-Sb_2O_4. We tested this possibility and effectively Δk_{ox} increases with the amount of α-Sb_2O_4 in the mixtures confirming our discussion above. This approach is valid for an empirical approach. For the moment it lacks fundamental grounds, namely the proof of a mechanism explaining the additional term Δk_{ox}.

The development of the remote control concept and the fact that it applies successfully to a very large number of data give provisionally some advantage to our model. There is clearly a need for further investigations for deciding on the best approach. This is the objective of the work we are presently doing.

In conclusion, the modified Mars–Van Krevelen equation incorporates a factor which reflects the changes, as a function of the experimental conditions, in the fraction of the catalyst surface which is undergoing the oxidation–reduction process. This modified equation represents more satisfactorily the experimental data when the reactant partial pressures, the temperature and the catalyst composition are changed. This equation reflects exactly (if only qualitatively) all the data accumulated on the selective oxidation of olefins to unsaturated aldehydes. All parameters in the modified equation have a physical meaning.

Because these parameters have a physical meaning, the equation can be used for interpreting experimental results when changes of catalysts formulations (e.g. nature of donor, proportion of components), changes of texture (e.g. contacts between phases) and gas phase compositions are made. Because of its fundamental bases, the equation can be used more safely for chemical engineering purposes as the formerly proposed equations.

References

[1] L.T Weng, P. Ruiz and B. Delmon, Stud. Surf. Sci. Catal., 72 (1992) 399.

[2] L.T. Weng and B. Delmon, Appl. Catal. A, 81 (1992) 141.

[3] F. Benyahia and A.M. Mearns, Appl. Catal., 70 (1991) 149.

[4] F. Benyahia and A.M. Mearns, Appl. Catal., 66 (1990) 383.

[5] R.S. Mann and D.K. Ko, J. Catal., 30 (1973) 276.

[6] I.Z. Onsan and D.L. Trimm, J. Catal., 38 (1975) 257.

[7] V. Cortés Corberán, A. Corma and G. Kremenic, Ind. Eng. Chem. Res. Dev., 24 (1985) 62.

[8] D.L. Hucknal, Selective Oxidation of Hydrocarbons, Academic Press, London, UK, 1974.

[9] D. Vande-Putte, S. Hoornaerts, F.C. Thyrion, P. Ruiz and B. Delmon, Fifth European Workshop Meeting On Selective Oxidation By Heterogeneous Catalysis, 6–7 November 1995, Berlin, Germany.

[10] S. Hoornaerts, D. Vande-Putte, F.C. Thyrion, P. Ruiz and B. Delmon, European Conference on Catalysis, Europacat-II, 3–8 September 1995, Maastricht, The Netherlands.