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Proposal of a new kinetic model based on the remote control mechanism to fit experimental data during the selective oxidation of isobutene to methacrolein on biphasic catalysts

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

[a] Unité des Procédés, Voie Minckeleers 1, 1348 Louvain-la-Neuve, Belgium
[b] Université Catholique de Louvain, Unité de Catalyse et Chimie des Matériaux Divisés, Place Croix du Sud 2 / 17, 1348 Louvain-la-Neuve, Belgium

Abstract

A new kinetic model based on the classical Mars–van Krevelen mechanism is proposed. The new model incorporates both the mechanism of site creation (via a remote control) and the catalytic reaction at the thus created (or controlled) active site. The model has been tested in the selective oxidation of isobutene to methacrolein on catalysts made of mechanical mixtures of α-Sb_2O_4 + MoO_3. The good fitting of the model with the experimental results shows that the remote control mechanism can explain the difficulties to represent the kinetics of allylic oxidation reactions by the traditional Mars–van Krevelen mechanism. The fraction of the surface of MoO_3 which selectively realises the oxidation via the oxidoreduction process depends on the degree of irrigation of MoO_3 by spillover oxygen produced on α-Sb_2O_4 and cannot be considered as constant. The possible use of the model for further progress in the kinetic description of selective oxidation reactions is briefly outlined.

Keywords: Kinetic model; Remote control mechanism; Isobutene; Methacrolein; Biphasic catalysts

1. Introduction

The kinetic models proposed in the literature for fitting experimental data in selective oxidation differ considerably, particularly for allylic oxidation. Striking differences are observed even when comparing only catalysts having qualitatively the same composition. The kinetic parameters (reaction orders, energy of activation, reduction and oxidation constants) derived from the conventional models turn out to be exceedingly sensitive to the proportion of the various elements and to the experimental conditions [1–3].

Mechanistic studies demonstrated that selective oxidations, and allylic oxidation, in particular, correspond to the sequence of (1) reduction of the catalyst surface by the hydrocarbon, followed by (2) reoxidation through molecular oxygen. The consequences should be that the kinetics obey the Mars–van Krevelen (MVK) equation [4]. However, the reasons why experimental results depart from the corresponding equations are not yet clear. Investigations done in our laboratory in the last years suggest new lines for a more accurate modelling of the kinetics of selective oxidation reactions.

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[*] Corresponding author.

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Multiphase catalysts always have a better performance, particularly in terms of selectivity and resistance to aging, than those containing only one phase. One of the increasingly more popular explanations of the superiority of multiphase oxide catalysts is the occurrence of a remote control mechanism (RCM) [5,6], but other explanations have been proposed [7–12]. Their common feature is that there is a 'job separation'. The argument is most simply presented for two-phase catalysts: one phase carries the active sites, and the other adjusts the activity and selectivity of this active phase. Migration of species from the second phase to the first is a common explanation of this adjustment, but the detailed mechanisms proposed for this migration differ.

The new kinetic equation that we derived is based on the RCM concept, because it emphasises the changes of the second phase due to the migrating species. We shall call this phase the *catalytically active* or acceptor phase (acceptor of mobile species coming from the first phase). A RCM operates when the first phase, which we call donor, dissociates molecular oxygen O_2 to spillover oxygen O_{so} and when this O_{so}, having migrated to the acceptor, reacts with its surface to give more active and more selective sites. This results in a steady-state situation in which selective sites are continuously created by the effect of O_{so} on the acceptor, but are also slowly deactivated because of a harmful side reaction occurring in parallel with the main one.

According to this concept, the creation of selective sites is a function, F_{rc}, of the proportions of donor (D) and acceptor (A) phase, and experimental conditions. The overall kinetic equation, incorporating both the mechanism of site creation and the catalytic reaction (in this work given by the classical MVK equation at each active site) then takes the following form:

$$\text{rate} = F_{rc}(\text{Donor}, \text{Acceptor}, p_{ox}, p_{HC}, T) \times (\text{Catalytic reaction}) \qquad (1)$$

where p_{ox} and p_{HC} represent, respectively, the oxygen and hydrocarbon pressures and T the temperature of the reaction.

The difficulty in oxidation reactions is that the oxygen and hydrocarbon pressures are present as variable in both parts of the equation (remote control on the one hand, and MVK on the other). Only in very special cases, where oxygen is not a reactant, but only has the role of creating selective sites through spillover (oxygen-assisted dehydrations), can relatively simple equations be obtained: F_{rc} is then the only term in the above equation which changes when the oxygen pressure changes. The fit between results and model is then excellent [13]. We consider here the general case where oxygen is an important parameter in both terms. This general case has been treated theoretically, describing the time-dependent transient effect when the experimental conditions are modified [14].

The above equation corresponds formally to reaction orders which change according to catalyst composition and reaction conditions. It explains why reaction orders change when the remote control operates.

The aim of the present work is therefore two-fold: (1) to show that significant changes in the reaction order are indeed observed when the RCM operates, and that these changes could have their origin in the irrigation of the acceptor by O_{so}; and (2) to show that the new kinetic equation we propose satisfactorily describes data gathered in rigorous experimental conditions. The parameters used in this model have a physical meaning. The reaction rate values obtained with the model will be compared with the experimental values.

The selective oxidation of isobutene to methacrolein has been used as test reaction. MoO_3 was selected because it behaves as a pure acceptor; α-Sb_2O_4, which is almost inactive in the reaction, is the donor. Biphasic catalysts were prepared by gently mixing separately prepared α-Sb_2O_4 and MoO_3 in different proportions. Reaction rates were measured in exactly the same experimental conditions for the pure oxides and the mixtures. The choice of MoO_3 and α-Sb_2O_4 is further justified by previous investigations demonstrating that MoO_3 and α-Sb_2O_4 do not form compound oxides nor contaminate each other. We independently demonstrated, using labelled oxygen (^{18}O), that superficial oxygen species could flow from α-Sb_2O_4 to MoO_3 [15].

2. Experimental

2.1. Preparation of pure 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 was 1 m^2/g for both oxides.

2.2. Mechanical mixtures of acceptor and donor

Biphasic catalysts were prepared by dispersing both powders in 200 ml of *n*-pentane. The suspension was agitated vigorously with an Ultra-Turrax equipment at 6000 rpm during 10 min and subsequently under ultrasound for 3 min; *n*-pentane was evaporated under reduced pressure, while continuing the agitation at 25°C. The solid was dried in air at 100°C overnight. Pure α-Sb_2O_4 and MoO_3 used for comparison were handled in the same way. The corresponding samples were not subjected to further calcination. The powders were pressed into wafers, then gently broken. The fraction between 315 and 500 μm was used.

2.3. Definition of the mass ratio (R_m)

The composition of the mixtures of α-Sb_2O_4 + MoO_3 was expressed as the mass ratio:

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

The mechanical mixtures used had the following compositions: $R_m = 0.0$; 0.25; 0.5; 0.75; and 1.0 ($R_m = 0.0$ being pure α-Sb_2O_4 and $R_m = 1.0$ pure MoO_3, respectively).

2.4. Catalytic activity measurement

2.4.1. Apparatus and catalytic test

Catalytic measurements were performed in a conventional fixed-bed reactor system at atmospheric pressure. The reactor was a Pyrex U-tube of 8 mm i.d. into which the catalyst was packed. The amount of catalyst varied from experiment to experiment in order to have conversions in the range of 5–15% (amount of catalyst between 300 and 1600 mg). The catalytic bed was deposited over a glass bed (spheres of 1 mm diameter) 10 cm high and under another glass bed 3 cm high. The reactant mixture was constituted of isobutene and oxygen diluted with helium. The total feed rate was 45 ml/min in all cases. Reactants and products were analysed by gas chromatography. 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 was always better than 90%.

2.4.2. Diffusional limitations into the pores of the catalysts

In order to evaluate the possible influence of diffusional phenomena, preliminary tests were realised with three granular fractions of the catalyst: 100–315 μm; 315–500 μm; and 500–800 μm. The reaction conditions were as follows: partial pressure of isobutene, 10.1 kPa; partial pressure of oxygen, 20.3 kPa; total pressure, 101.3 kPa; the diluent being helium. The reaction temperatures were 380, 400, 440 and 460°C. The reaction rates were the same for all catalyst granulometries, within the precision of the experiments. This indicated that intraparticle diffusion had no influence on the rates observed [16].

2.4.3. *Standard test varying the partial pressure of oxygen*

The reactor was first fed with a mixture corresponding to a partial pressure of oxygen of 30.4 kPa, a partial pressure of isobutene of 10.1 kPa and a partial pressure of helium of 60.8 kPa, and the reactor was stabilised to the desired temperature. Analysis of reactants and products were realised during 2 h. After that, the 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 70.9 kPa in order to maintain the total pressure at the value of the atmospheric pressure. Analysis were realised during 2 h and then the partial pressure of oxygen was decreased to a lower value with a corresponding increase of the helium pressure. The same procedure as above was followed for other partial pressures of oxygen: 10.1, 5.1, 2.5 and 1.0 kPa. The measurements were made at 400°C.

2.4.4. *Standard test varying the partial pressure of isobutene*

The same procedure as in section 2.4.3 was followed to measure the influence of the isobutene pressure. The partial pressure of oxygen was fixed at 10.1 kPa, the partial pressure of isobutene at 2.5 kPa and the mixture balanced with helium at 88.7 kPa. After stabilisation of the temperature, samples were taken during 2 h. The same procedure was followed with the partial pressure of isobutene increased to 5.1, 10.1 and 20.3 kPa with the total pressure always maintained at 101.3 kPa. The reaction temperature was 400°C.

3. Modelling of the kinetics equation

The fraction ρ' of the acceptor surface, which permits the reduction–oxidation process of the selective catalytic reaction, depends on the relative amount of donor added to the acceptor (as characterised by R_m). It also depends on the oxygen pressure which, through the dissociation to O_{so}, modifies the concentration of O_{so} on the acceptor surface and, consequently, the rate of reaction of O_{so} with the acceptor surface. Since the active sites on the acceptor get deactivated by too deep a reduction by the isobutene in the unwanted side reaction, the pressure of isobutene, p_{C4}, also influences this fraction ρ'.

Using the function F_{rc}, which it is not necessary to define here, we write finally:

$$\rho' = F_{rc}(R_m, p_{ox}, p_{C4}, T) \tag{2}$$

Let us consider a given surface area of the acceptor undergoing the selective reduction–oxidation process, namely a given area of *selective* surface (S'). The reduction–oxidation mechanism corresponds to 2 steps:

$$S'_{ox} + \text{isobutene} \rightarrow S'_{red} + \text{methacrolein} + H_2O$$

$$S'_{red} + O_2 \rightarrow S_{ox}$$

in which S'_{red} and S'_{ox} represent the parts of S' which are reduced and oxidised, respectively. Let the rate of selective oxidation per unit surface area of S' be designated by r'. At steady state, this is equal to the rates of reduction by isobutene (r'_{red}) and oxidation by O_2 (r'_{ox}), respectively. If α'_{red}, α'_{ox}, k_{red} and k_{ox} are, respectively, the fractions of S' reduced and oxidised and the corresponding rate constants per unit surface area of S'_{ox} and S'_{red}:

$$r'_{red} = k_{red}\, p_{C4}\, \alpha'_{ox} \tag{3}$$

$$r'_{ox} = k_{ox}\, p_{ox}^{1/2}\, \alpha'_{red} \tag{4}$$

(if limited by dissociation of oxygen)

The steady state on S' will give us the classical MVK equation. At the steady state: $r'_{re} = r'_{ox}$, then

$$k_{red}\, p_{C4}\, \alpha'_{ox} = k_{ox}\, p_{ox}^{1/2}\, \alpha'_{red}$$

or

$$k_{red}\, p_{C4}\, \alpha'_{ox} = k_{ox}\, p_{ox}^{1/2}\, (1 - \alpha'_{ox}).$$

Rearranging these relations gives the rate of selective oxidation r' per unit surface area of the *selective* part of the catalyst,

$$r' = r'_{red} = r'_{ox} = \frac{k_{red}\, p_{C4} \cdot k_{ox}\, p_{ox}^{0.5}}{k_{red}\, p_{C4} + k_{ox}\, p_{ox}^{0.5}} \tag{5}$$

To obtain the rate r_t (namely the total rate) for a given amount of catalyst of a given composition R_m, where the acceptor surface area is S, r' has to be multiplied by S', namely $\rho' S$

$$r_t = S \cdot \rho' \frac{k_{red}\, p_{C4} \cdot k_{ox}\, p_{ox}^{0.5}}{k_{red}\, p_{C4} + k_{ox}\, p_{ox}^{0.5}} \qquad (6)$$

where ρ' is given by the 'remote control relation F_{rc}' (2).

The rate of reaction *per unit weight* ('specific') of *mixture* (r_{sm}) would be obtained by replacing S by $R_m \cdot S_s$, with S_s the specific area of the acceptor. For describing a series of experiments made with the same amount of catalyst (of different compositions), r_{sm} is the equation that should be used. This is the standard equation for modelling the kinetics of a catalytic reaction on multiphase catalysts.

For evaluating the relevance of the kinetic model proposed in this article, a slightly different equation must be used, because the overall quantity of catalyst changes from experiment to experiment, in order to keep the conversion at low values. It is then more convenient to calculate the rate per unit surface area of the acceptor (MoO_3) contained in the mixture (symbol: r_a).

$$r_a = \rho' \frac{k_{red}\, p_{C4} \cdot k_{ox}\, p_{ox}^{0.5}}{k_{red}\, p_{C4} + k_{ox}\, p_{ox}^{0.5}} \qquad (7)$$

Calculated in this way, the rate measured under given conditions (p_{C4}, p_{ox}, T) will directly reflect the variations of ρ' due to the action of spillover oxygen and, consequently, the variations of the function F_{rc} of Eq. (2).

It ensues that, working with the *pure acceptor*, one can, in principle, determine from Eq. (7) the *relative* values of k_{red} and k_o from the variations of r_a as a function of p_{C4} and p_{ox} for pure MoO_3, because the fraction ρ' of the surface permitting the selective reduction–oxidation process is not influenced by the remote control effect (pure MoO_3 is only acceptor). We shall call this fraction ρ'_1 (ρ' for $R_m = 1$). The value of ρ'_1 is unknown. The results with R_m different from 1.0 will correspond to ratios of the corresponding ρ' to ρ'_1. This can be calculated from Eq. (7). If our model is correct, the value of ρ', which reflects the fraction of S which is active, should increase when the proportion of the donor increases, namely when $(1 - R_m)$ increases. This is what we wish to demonstrate in this paper.

For comparison, we also attempted to represent the results by the usual empirical type of equation: $r_a = kp_{C4}^n$ and $r_a = kp_{ox}^m$.

3.1. 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 minimises 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 determined by the model are those for which the function $F' = F/n$ with $F = \Sigma(V_{model} - V_{exp})^2$ and 'n' the number of experiments, is smaller than 10^{-1}.

4. Results

4.1. Empirical orders for oxygen and isobutene

In the mixtures, *both empirical orders decrease* when the amount of α-Sb_2O_4 in the mixtures increases (Table 1).

Table 1
Oxygen and isobutene empirical partial pressure orders

	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%)
Oxygen order	0.53	0.36	0.33	0.26
Isobutene order	0.75		0.08	

Table 2

Values of k_{red}, k_{ox} and F, obtained by fitting the experimental reaction rate values to the model of Eq. (7) considering $\rho'/\rho'_1 = 1$

Catalysts	ρ'/ρ'_1	$k_{red} \cdot 10^3(\mathrm{Pa}^{-1})$	$k_{ox} \cdot 10^3(\mathrm{Pa}^{-1})$	$F = \Sigma(V_{model} - V_{exp})^2$
MoO_3 (100%)	1.0	2.6	40.0	0.0223
MoO_3 (75%) + α-Sb_2O_4 (25%)	1.0	73.8	6.9	0.0032
MoO_3 (50%) + α-Sb_2O_4 (50%)	1.0	Non convergence [a]	Non convergence	Non convergence
MoO_3 (25%) + α-Sb_2O_4 (75%)	1.0	21.5	74.1	0.0312

[a] Non-convergence indicates that, after 200 iterations, the criterion presented in section 3.1 is not satisfied.

4.2. Fitting of the parameters

In Table 2, we present the results obtained by fitting the parameters with the model presented in Eq. (7), but considering $\rho'/\rho'_1 = 1$ (namely using the classical MVK model). It is clear that: (1) there is no correlation between the k_{red} and k_{ox} values when the amount of α-Sb_2O_4 changes; and (2) no convergence of the algorithm has been obtained for the mixtures containing 50% of α-Sb_2O_4. Table 3 presents the results obtained when the values of k_{red} and k_{ox} are set as identical to those obtained with pure MoO_3 and ρ'/ρ'_1 is allowed to change. In this case, results show that: (1) convergence is observed in all cases; and (2) the fitting gives values which increase regularly when the amount of α-Sb_2O_4 in the mixtures increases. Comparison of Tables 2 and 3 shows that the F values are more favourable in Table 3.

Fitting obtained without setting a priori the parameters k_{ox} and k_{red} are presented in parentheses in Table 3. The fitting process gives very dispersed values. It is clear that the results are not numerous nor precise enough to permit the simultaneous determination of the 3 unknown parameters (ρ', k_{red} and k_{ox}).

5. Discussion and conclusions

The changes observed in the empirical orders is the logical consequence of the RCM. The variations reflect in a complicated way the double influence of the partial pressures of the reactants on: (1) the fraction of the surface which undergoes the reduction–oxidation process; and (2) the rate of the reduction–oxidation process itself. On the other hand, the fact that the classical MVK model is not able to fit correctly the parameters when MoO_3 is mixed with α-Sb_2O_4 clearly shows that this model is not adequate and that an additional phenomenon is occurring during the reaction. We propose that this is the RMC.

However, these results rest on a limited set of measurements. It is impossible to claim that the good fit of the new model demonstrates the validity of the RCM. This validity is supported in other publications [17–20]. Our results *sim-*

Table 3

Values of k_{red}, k_{ox} and ρ'/ρ'_1 and F, obtained by fitting the experimental reaction rate values to the model of Eq. (7)

Mechanical mixtures	ρ'/ρ'_1		$k_{red} \cdot 10^3(\mathrm{Pa}^{-1})$		$k_{ox} \cdot 10^3(\mathrm{Pa}^{-1})$		$F = \Sigma(V_{model} - V_{exp})^2$
MoO_3 (100%)	1.00	(0.008)	2.6	(47.9)	40.0	(41.90)	0.0223
MoO_3 (75%) + α-Sb_2O_4 (25%)	0.56	(0.016)	2.6	(4.4)	40.0	(110.80)	6.1×10^{-4}
MoO_3 (50%) + α-Sb_2O_4 (50%)	1.04	(0.016)	2.6	(36.4)	40.0	(3.70)	0.0382
MoO_3 (25%) + α-Sb_2O_4 (75%)	3.79	(0.064)	2.6	(8.4)	40.0	(4.15)	0.0585

The values of k_{red} and k_{ox} are set to be equal to those obtained from the data with pure MoO_3. Values of F correspond to this fitting. In parenthesis are values obtained fitting simultaneously k_{red}, k_{ox} and ρ'/ρ'_1.

ply prove that a model based on this mechanism simultaneously (1) fits the experimental result in a self-consistent way and (2) fully respects the universally accepted features of the MVK mechanism.

If we accept the validity of the RCM, the results are those expected. The values obtained for ρ'/ρ'_1 grow when the amount of the donor phase (α-Sb_2O_4) increases. The increase is proportionally larger for $R_m = 0.25$ (75% Sb_2O_4). This is logical: there are then about three times more α-Sb_2O_4 than MoO_3 particles. MoO_3 becomes then surrounded by α-Sb_2O_4 particles (probably more than 6, at least if the distribution of particles in the mixture is statistically uniform). All the surface of the MoO_3 particles can then be efficiently 'irrigated' by spillover oxygen.

Referring to Table 1, if we accepted that the changes of reaction orders reflect changes in the MVK mechanism, the results would lead to an absurd conclusion, namely that the oxidoreduction of a same phase, namely MoO_3, would exhibit different kinetics of reduction or oxidation according to experimental conditions. It would be still more difficult to accept that the reaction orders of both reduction and oxidation change so drastically (e.g., from nearly 0 for $R_m = 0.5$ to 0.75 from $R_m = 1$, when the reduction step is considered). In addition, the fractional order obtained cannot be related to any mechanistic feature. In this perspective, the results would rather suggest that the MVK mechanism is not valid. This is difficult to accept taking account of the innumerable experimental results demonstrating that this mechanism is fundamental in allylic oxidation. Our results clearly show that a very important factor is forgotten when using the classical equation derived from the MVK mechanism.

The essential feature of the new model is the *separation of the kinetic equation in two terms*, one of which is the MVK term. This makes possible, in principle, for the first time, to relate *quantitatively* (or, at least, semi-quantitatively) the kinetic parameters of the MVK mechanism to independent experiments aimed at directly measuring the rates of reduction and reoxidation (e.g., pulse or TAP experiments).

The model also offers the possibility to identify the changes in the fraction of the active phase (acceptor) which are caused by all experimental parameters: oxygen and hydrocarbon pressure, temperature, catalyst composition, catalyst fine structure (dispersion of each phase, contact between phases). The concept of separation into two terms, one of which is the MVK term, is not only valid if the RCM operates, but also if other mechanisms are believed to operate (e.g., those mentioned in the introduction). The present article emphasises the influence of catalyst composition. This parameter is isolated from other possible ones (e.g., changes of dispersion). The separation of terms permits, in principle, the study of the influence of those additional terms.

If we accept that the RCM really operates in the present case, experimental measurements could approach an accurate determination of the influence of all parameters featured in the function F_{rc} expressing the dependence of ρ' on these parameters. As indicated in the introduction, comprehensive models have been developed [13,14]. The most elaborate one [14], unfortunately, is too complicated (with respect to the computational aspects) to be used directly in the general case. The approximation given by equation [7] permits an approximate determination of some parameters (e.g., temperature, oxygen pressure) and would thus make the search for satisfactory values in comprehensive models much easier.

In a simpler approach, the values of ρ'/ρ'_1 presented in Table 3 can be used to model the influence of O_{so} on F_{rc} during the reaction. An order of 1.65 can be obtained for the variation of formal ρ'/ρ'_1 as function of the amount of α-Sb_2O_4 in the mixtures, namely an increase more than proportional to the quantity of α-Sb_2O_4. This order represents the global influence of the O_{so} emitted by α-Sb_2O_4.

This approach is insufficient, however, be-

Table 4
Values of k_{red}, k_{ox}, k_o and F, obtained by fitting the experimental reaction rate values to the model of Eq. (7) considering $\rho'/\rho'_1 = k_o p_{ox}^{0.5}$

Catalysts	k_o		$k_{red} \cdot 10^3 (Pa^{-1})$	$k_{ox} \cdot 10^3 (Pa^{-1})$	$F = \Sigma (V_{model} - V_{exp})^2$	
MoO_3 (75%) + α-Sb_2O_4 (25%)	0.047	(0.003)	2.6	40.0	0.0055	(0.0103)
MoO_3 (50%) + α-Sb_2O_4 (50%)	0.097	(0.006)	2.6	40.0	0.0516	(0.0810)
MoO_3 (25%) + α-Sb_2O_4 (75%)	0.342	(0.023)	2.6	40.0	0.0942	(0.256)

The values of k_{red} and k_{ox} are set to be equal to those obtained from experience with pure MoO_3. In parentheses are values obtained using the equation $\rho'/\rho'_1 = k_o p_{ox}^{1.0}$.

cause the amount of O_{so} flowing onto the surface of MoO_3 depends on other parameters (in particular, oxygen and hydrocarbon partial pressures, number of contacts between α-Sb_2O_4 and MoO_3, temperature, etc. [21]). A substantially better agreement is obtained when separating the influence of increasing the amount of donor from that of increasing the oxygen pressure in the production of more O_{so}. Let us assume, as a first approximation, that ρ'/ρ'_1 is proportional to $p_{ox}^{0.5}$ (taking into account the dissociation of O_2 to O_{so} on the donor): $\rho'/\rho'_1 = k_o p_{ox}^{0.5}$. The parameter k_o should then reflect more precisely than the formal order 1.65 (or other equation as $\rho'/\rho'_1 = k_o p_{ox}^{1.0}$) the influence of the amount of α-Sb_2O_4. The values of k_o in Table 4 indeed show that k_o increases with increasing R_m. It is interesting to note that the k_o values obtained when considering the dissociation of O_2 represent better the experimental data.

The selectivity of the reaction (or the fraction of the surface of the acceptor which is irrigated by O_{so}) will also depend on the coupling of other simultaneous phenomena which themselves are dependent from the experimental conditions, namely: (1) the ability of the donor to activate oxygen to O_{so}; (2) the facility of the catalytic oxides to allow the migration of O_{so} (rate of diffusion); (3) the facility of O_{so} to react with the surface of the acceptor; (4) the nature of oxygen species formed on the donor; (5) the reactivity of the hydrocarbon molecules with the different oxygen species which are formed on the donor; (6) the participation of O_{so} in the reaction mechanism, etc. Taking this into account, it is not excluded that, under precise reaction conditions, the fraction ρ' be less than ρ'_1, explaining values lower than 1. However, it is necessary to emphasise that, in this case, selectivity is much higher than observed in pure acceptor, as has largely been discussed previously [5,6]. We admit that the analysis of the new kinetic model must still be refined in order to account for all the details of the variation of ρ'/ρ'_1 as presented in the tables.

In summary, the new model offers good prospects for a satisfactory modelling of experimental data. It is compatible with the remote control mechanism. All the parameters of the model have a precise physical meaning.

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