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Catalysis Today 32 (1996) 11-20

CATALYSIS TODAY

The transient response technique for the study of hydrocarbon oxidation on metal oxides: Simulation of the responses for various propene oxidation mechanisms

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Abstract

Partial differential equations, describing the consumption of reactants and the formation of products, have been solved numerically for a step change from inert to reactant feed considering different variants of propene oxidation mechanisms. The response features and their dependency on the rate limiting step have been rationalised in terms of conclusions, which can serve as general guidelines for mechanistic interpretation of experimental transients from hydrocarbon oxidation over metal oxides. Though the response pattern is characteristic of the rate limiting step, it is demonstrated that different variants of mechanisms can give identical response features. In that case complementary investigation with other techniques, or more detailed mathematical analysis is necessary.

Keywords: Transient response; Simulation; Oxidation; Propene; Mechanism

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1. Introduction

A common way to investigate the kinetics and the related mechanism of a heterogeneously catalysed reaction is to use the method given by Hougen and Watson [1], i.e., fitting steady state data to an assumed reaction mechanism. The procedure is tedious, since a large number of data points have to be collected at stationary conditions. The transient response method, which has been reviewed by Kobayashi and Kobayashi [2], and Bennet [3], is a useful tool providing complementary information about the mechanism and kinetics of the reaction. As will be demonstrated in this contribution, a benefit of a study of transients is that a few experiments, even one, can give much more information about the mechanism than is derivable from a similar number of stationary measurements. Therefore, transient experiments are useful, especially for preliminary screening to definitely limit the number of possible mechanisms that are selected for further evaluation. This approach is useful when investigating new catalysts and/or reactions.

Using a differential reactor, Kobayashi [4] has simulated the responses to step changes considering various model reactions and has related the shape of the responses to the reaction mechanism. However, Kobayashi did not give the responses of the reactants and did neither

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PII S0920-5861(96)00177-0

directly address oxidation over metal oxides. The latter type of reaction is special in the sense that one reactant, namely oxygen, is initially present at the surface in high concentration. In the present work we report theoretical responses of products and reactants to a step change from inert to reactant feed, which have been simulated considering various types of mechanisms for propene oxidation. For the purpose of rationalisation, the rate constants have been chosen so that one step clearly becomes rate determining when stationary conditions are approached. The mechanisms of propene oxidation over molybdates and antimonates have indeed been well investigated [5]. In this regard it is worthy of note that the results of the present calculations, using propene oxidation only as a model reaction, admit the rationalisation of the transient behaviour and the response shapes to give conclusions which are valid irrespective of the specific hydrocarbon and the catalyst type.

2. Calculations

Assuming that the gas velocity through a plug flow reactor does not change, i.e., low conversion, large content of an inert, and/or no molar changes due to reaction, the following system of partial differential equations describes the system (for notations see Table 1):

$$\frac{\partial p_i}{\partial t} = -\frac{u_0}{\varepsilon}\frac{\partial p_i}{\partial x} + \frac{RT\rho_B}{\varepsilon}\sum_{j=1}^{m} r_{ij} \tag{1}$$

$$\frac{\partial \theta_k}{\partial t} = \frac{1}{n_k}\sum_{j=1}^{m} r_{kj} \tag{2}$$

By using a simple approximation of the spatial derivative Eq. (1) becomes:

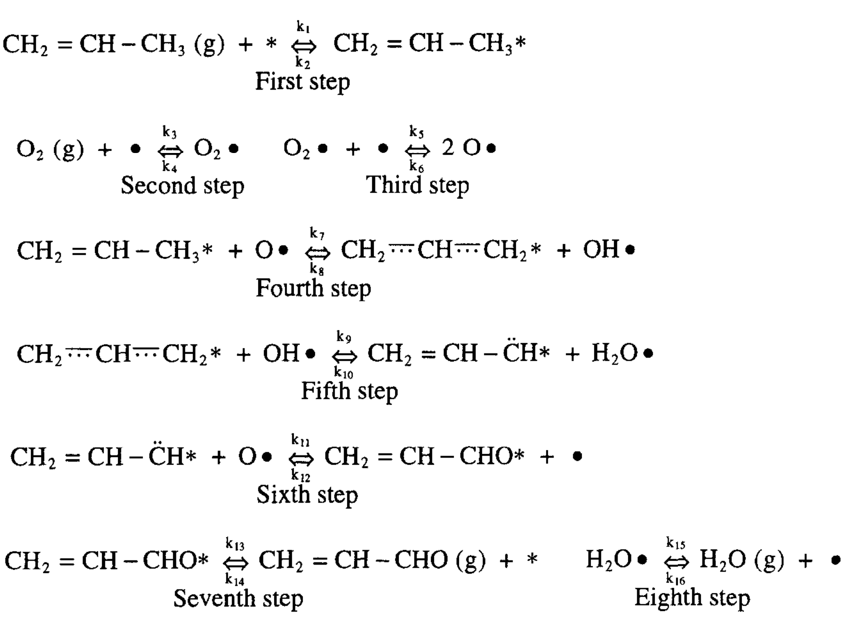
$$\frac{\partial p_i}{\partial t} = -\frac{u_0}{\varepsilon}\frac{p_i^x - p_i^{x-\Delta x}}{\Delta x} + \frac{RT\rho_B}{\varepsilon}\sum_{j=1}^{m} r_{ij} \tag{3}$$

i.e., a tanks-in-series model. A set of ordinary differential equations now describe the system. The number of tanks were twenty in the simulations. Other parameter values are given in Table 1. The selected values for the reaction parameters are of reasonable magnitude for partial oxidation catalysts. However, the exact parameter values are not limiting for the present purpose to focus not on the estimation of kinetic constants, but on the correlation between response features and mechanistic details.

To verify the rate limiting step, each step was disturbed twice by decreasing and increasing the selected constant by a factor one half and two, respectively. In the case of a reversible step

Table 1
Parameter values used in the simulations

n_k, number of sites available for surface species k		mol/g
n_1, number of sites of type 1, denoted $*$ and $*'$	$5.16 \cdot 10^{-5}$	mol/g
n_2, number of sites of type 2, denoted $\cdot$ and $\cdot'$	$1.32 \cdot 10^{-4}$	mol/g
p_i, partial pressure of species i		atm
R, gas constant	82.057	atm · cm^3/mol/K
Reactor length	0.5	cm
r_{ij}, rate of formation of gaseous species i in reaction j		mol/g/min
r_{kj}, rate of formation of surface species k in reaction j		mol/g/min
T, temperature	753.15	K
t, time		min
Total pressure	1	atm
u_0, superficial gas velocity	1592	cm/min
x, distance from inlet of reactor		cm
ϵ, void fraction of catalyst bed	0.45	–
θ_k, fractional coverage with surface species k		–
ρ_B, bulk density of catalyst bed	1.538	g/cm^3



$$CH_2=CH-CH_3\,(g) + * \underset{k_2}{\overset{k_1}{\Leftrightarrow}} CH_2=CH-CH_3*$$
First step

$$O_2\,(g) + \bullet \underset{k_4}{\overset{k_3}{\Leftrightarrow}} O_2\bullet \qquad O_2\bullet + \bullet \underset{k_6}{\overset{k_5}{\Leftrightarrow}} 2\,O\bullet$$
Second step Third step

$$CH_2=CH-CH_3* + O\bullet \underset{k_8}{\overset{k_7}{\Leftrightarrow}} CH_2\overset{\cdots}{-}CH\overset{\cdots}{-}CH_2* + OH\bullet$$
Fourth step

$$CH_2\overset{\cdots}{-}CH\overset{\cdots}{-}CH_2* + OH\bullet \underset{k_{10}}{\overset{k_9}{\Leftrightarrow}} CH_2=CH-\ddot{C}H* + H_2O\bullet$$
Fifth step

$$CH_2=CH-\ddot{C}H* + O\bullet \underset{k_{12}}{\overset{k_{11}}{\Leftrightarrow}} CH_2=CH-CHO* + \bullet$$
Sixth step

$$CH_2=CH-CHO* \underset{k_{14}}{\overset{k_{13}}{\Leftrightarrow}} CH_2=CH-CHO\,(g) + * \qquad H_2O\bullet \underset{k_{16}}{\overset{k_{15}}{\Leftrightarrow}} H_2O\,(g) + \bullet$$
Seventh step Eighth step

Scheme 1. First mechanism for oxidation of propene.

both the forward and the backward rate constants were changed to keep the ratio constant.

3. Results and discussion

In all the cases given below, the shape of each response was the same throughout the reactor, i.e., it was independent of the conversion. The responses shown in the figures are those from the outlet of the reactor.

3.1. Oxidation of propene to acrolein, first model

The first model that will be considered is depicted in Scheme 1 and follows the early mechanism that was proposed by Adam and Jennings [6] for propene oxidation over bismuth molybdate and cuprous oxide. In Fig. 1 are the responses given to a step change from inert to inert with propene and oxygen for different sets of rate constants. The values of the rate constants are given in Table 2. In all simulations the oxygen sites are initially fully covered, which is in agreement with the general belief that lattice oxygen species participate in partial oxidation pathways [7]. When the adsorption of propene is rate determining (Fig. 1a), the response of propene is instantaneous compared to the mean residence time. Since there is no initial possibility for oxygen to adsorb, the response of oxygen instantaneously reaches the

Table 2
Non default values [a] of the rate constants [b] that were used for the responses in Fig. 1

Rate determining step	Rate constants with non default values	
First	$k_1 = 1 \cdot 10^{-3}$	
Second	$k_3 = 1 \cdot 10^{-3}$	$k_1, k_5, k_7, k_9, k_{11}, k_{13}, k_{15} = 1 \cdot 10^{-2}$
Fourth	$k_7 = 1 \cdot 10^{-5}$	
Sixth	$k_{11} = 1 \cdot 10^{-5}$	
Eighth	$k_{15} = 1 \cdot 10^{-5}$	$k_1, k_3, k_5, k_7, k_9, k_{11}, k_{13} = 1 \cdot 10^{-2}$

[a] Default values: forward rate constants $1 \cdot 10^{-1}$, and backward rate constants $1 \cdot 10^{-9}$.

[b] The units of the rate constants are in accordance with the units in Table 1.

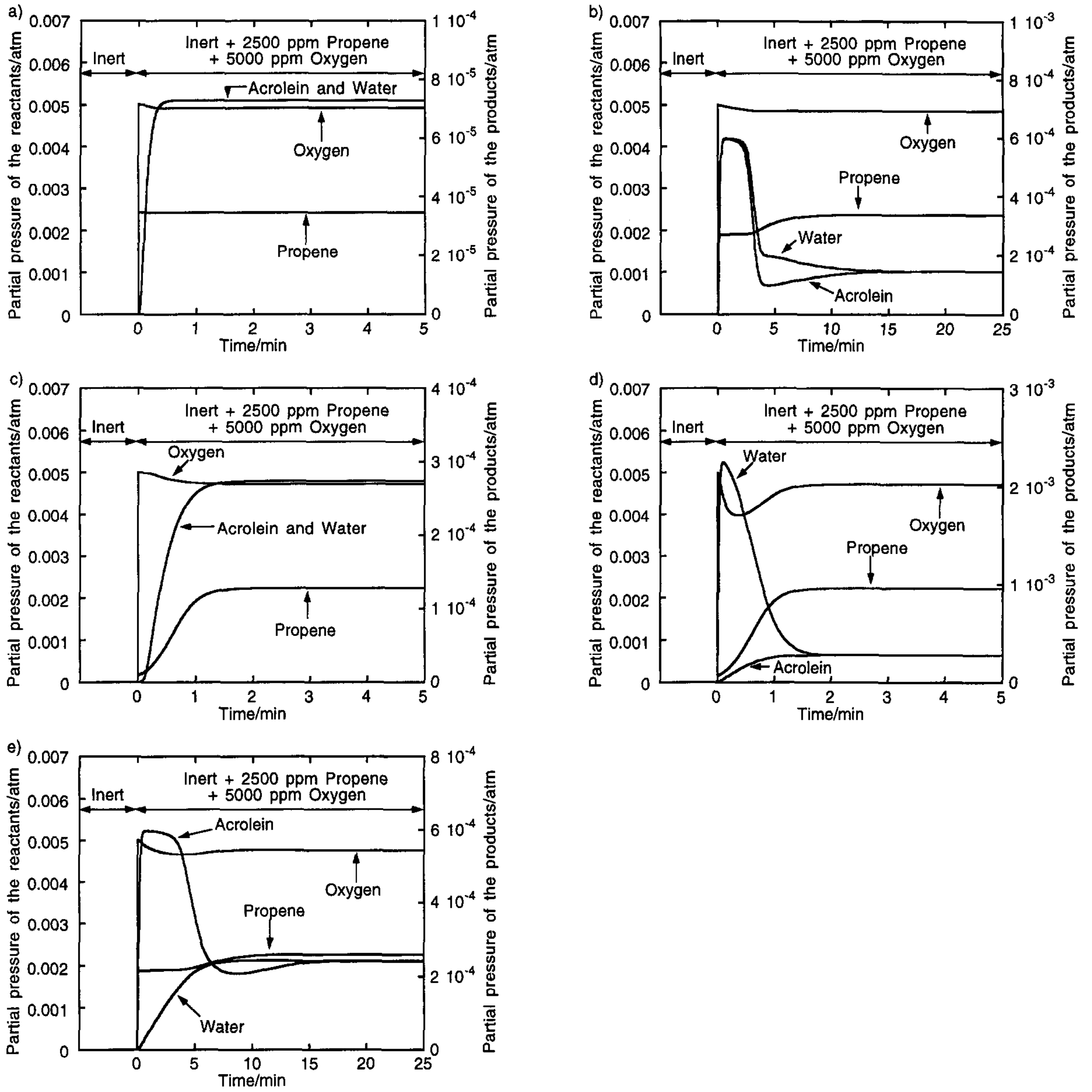


Fig. 1. Responses of reactants and products (first model) when the rate limiting step is as follows: (a) first step, adsorption of propylene; (b) second step, adsorption of oxygen; (c) fourth step, formation of allylic species; (d) sixth step, oxygen insertion; and (e) eighth step, desorption of water. The rate constants are given in Table 2. The oxygen sites are initially fully covered.

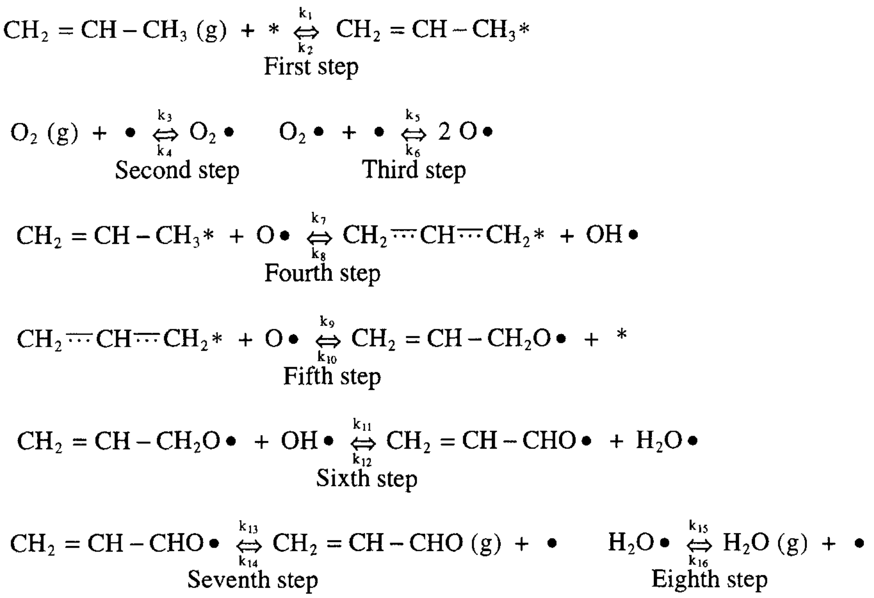
inlet value, but then starts to decrease because adsorption begins. The responses of acrolein and water are steep, because the surface coverage with propene reaches the stationary value very fast due to the slow adsorption rate and rapid surface and desorption steps. The fact that the responses of acrolein and water cannot be distinguished from each other is because both products are formed subsequent to the rate limiting step and the rates of the subsequent steps are equal also during the transient period.

When the adsorption of oxygen is rate determining (Fig. 1b), the response of propene is instantaneous up to a plateau, since all surface and desorption steps are rapid. After about 3 minutes, the pressure of propene increases to a higher level due to exhaustion of the initial oxygen species and the oxygen replenishment is the slow step. The response of oxygen can be explained like in the previous case, i.e., all oxygen sites are initially occupied. The partial pressure of acrolein and water increase initially to a high level because the surface coverage with atomic oxygen is high, and all steps involved are fast. The pressures start to decrease when there is lack of atomic oxygen. The difference in the response of acrolein and water between 3 and 15 minutes can be explained by the formation of water requires one oxygen atom (fourth step), while acrolein formation requires yet another oxygen (sixth step). Therefore, the decrease in the partial pressure of acrolein is temporarily the highest. This can, of course, not go on for any longer time, so the pressure of acrolein starts to increase up to the level of the water pressure, since equimolar amounts of water and acrolein are formed.

When the dissociation of oxygen is rate determining (third step), the shapes of the responses are of the same type as shown in Fig. 1b and can be explained in the same way and are therefore not shown.

For the data in Fig. 1c the rate constant used for propene adsorption is greater than that for the data in Fig. 1b. Consequently, the level of the instantaneous part of the propene response is very low and the partial pressure of propene shows a drawn out increase until the surface site for propene adsorption is almost fully covered. Because the fourth step (first hydrogen abstraction) is slow, the coverage with the allylic intermediate increases during an extended period and so do the responses of acrolein and water. The trends are the same when the fifth step (second hydrogen abstraction) is rate determining.

The responses of propene and acrolein in Fig. 1d when the insertion of oxygen (sixth step) is rate determining can be explained as for the previous case. Because the formation of water is complete already after the fifth step, the rate determining step has initially no influence on the formation of water, and the response of water reaches a high value. By the same reason the partial pressure of oxygen decreases to quite a low level. At later stage, because of the



$$\mathrm{CH_2=CH-CH_3\,(g)} + * \underset{k_2}{\overset{k_1}{\Leftrightarrow}} \mathrm{CH_2=CH-CH_3}*$$

First step

$$\mathrm{O_2\,(g)} + \bullet \underset{k_4}{\overset{k_3}{\Leftrightarrow}} \mathrm{O_2}\bullet \qquad \mathrm{O_2}\bullet + \bullet \underset{k_6}{\overset{k_5}{\Leftrightarrow}} 2\,\mathrm{O}\bullet$$

Second step Third step

$$\mathrm{CH_2=CH-CH_3}* + \mathrm{O}\bullet \underset{k_8}{\overset{k_7}{\Leftrightarrow}} \mathrm{CH_2}\overset{\cdots}{-}\mathrm{CH}\overset{\cdots}{-}\mathrm{CH_2}* + \mathrm{OH}\bullet$$

Fourth step

$$\mathrm{CH_2}\overset{\cdots}{-}\mathrm{CH}\overset{\cdots}{-}\mathrm{CH_2}* + \mathrm{O}\bullet \underset{k_{10}}{\overset{k_9}{\Leftrightarrow}} \mathrm{CH_2=CH-CH_2O}\bullet + *$$

Fifth step

$$\mathrm{CH_2=CH-CH_2O}\bullet + \mathrm{OH}\bullet \underset{k_{12}}{\overset{k_{11}}{\Leftrightarrow}} \mathrm{CH_2=CH-CHO}\bullet + \mathrm{H_2O}\bullet$$

Sixth step

$$\mathrm{CH_2=CH-CHO}\bullet \underset{k_{14}}{\overset{k_{13}}{\Leftrightarrow}} \mathrm{CH_2=CH-CHO\,(g)} + \bullet \qquad \mathrm{H_2O}\bullet \underset{k_{16}}{\overset{k_{15}}{\Leftrightarrow}} \mathrm{H_2O\,(g)} + \bullet$$

Seventh step Eighth step

Scheme 2. Second mechanism for oxidation of propene.

build-up of high concentration with $CH_2 = CH - \ddot{C}H*$, the pressure of water has to decrease and that of oxygen must increase. When the desorption of acrolein (seventh step) is rate determining, the responses are similar.

The pressure of acrolein is initially high when the desorption of water is rate determining (Fig. 1e), since this step does not affect initially the rate of acrolein formation. Due to the build-up with water on oxygen sites, the partial pressure of acrolein starts to decrease. The fact that the oxygen pressure only decreases slightly during the first 5 minutes is due to water blocks the oxygen sites. The increase of oxygen pressure after five minutes is therefore also small. Between 7 and 15 minutes, the partial pressure of water is higher than that for acrolein. The same behaviour is apparent in Fig. 1b, and can be explained as due to acrolein formation involves two oxygen species compared with one species in water formation.

3.2. Oxidation of propene to acrolein, second model

In the first model it was assumed that the insertion of oxygen occurs after the second hydrogen abstraction. According to the mechanism by Grasselli and co-workers [5,7], the insertion of oxygen on molybdates and antimonates occurs immediately after the abstraction of the first α-hydrogen atom. Such a mechanism, assuming separate adsorption and oxygen sites, is shown in Scheme 2. For this second

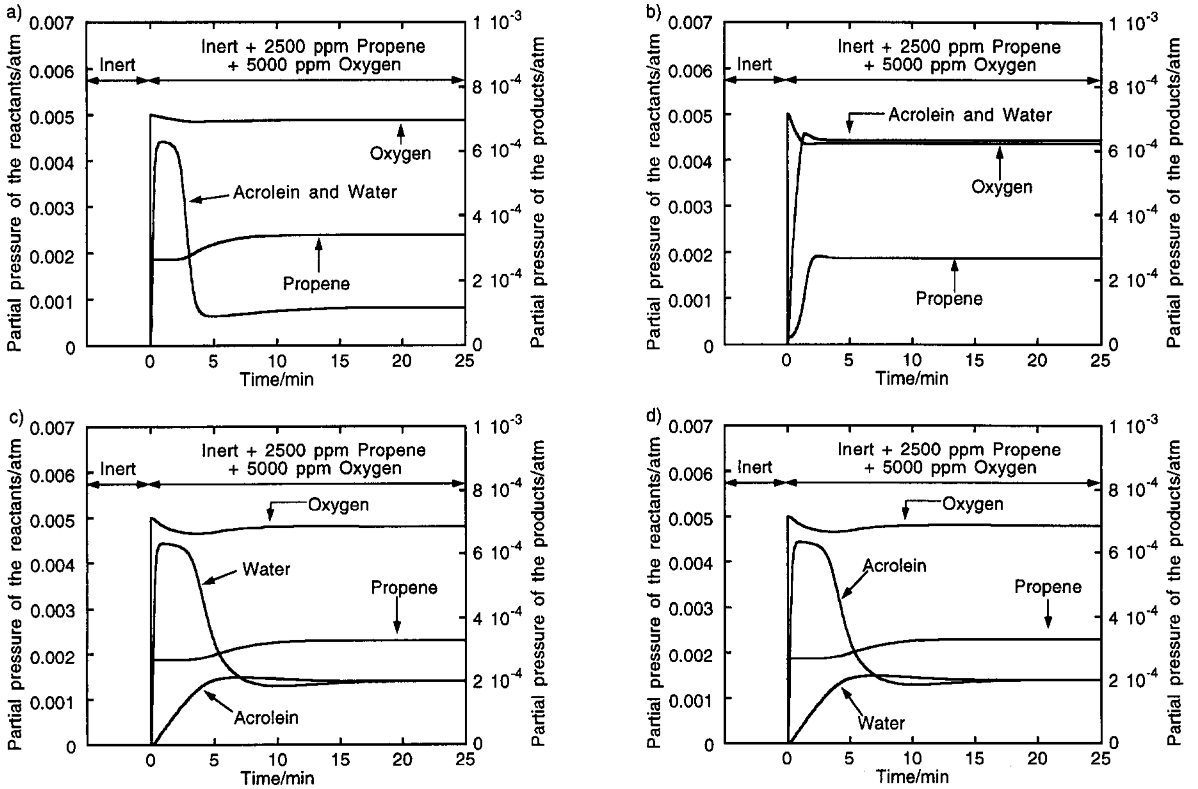


Fig. 2. Responses of reactants and products (second model) when the rate limiting step is as follows: (a) second step, adsorption of oxygen; (b) sixth step, formation of acrolein and water; (c) seventh step, desorption of acrolein; and (d) eighth step, desorption of water. The rate constants are given in Table 3. The oxygen sites are initially fully covered.

model, calculations were performed using the rate constants given in Table 3 with various rate determining steps.

When the adsorption of propene is rate determining, the shapes of the responses are the same as those in Fig. 1a for the first model and can apparently be explained in the same way. In Fig. 2a are the responses when the adsorption of oxygen is rate determining. The response features are very similar to those in Fig. 1b for the first model, except for the responses of acrolein and water being identical in Fig. 2a. The reason is, in contrast to the first model, that water and acrolein are both formed in the same step.

When either the first hydrogen abstraction or the oxygen insertion is rate determining, the shapes of the responses are the same as in Fig. 1c and are therefore not shown. Since there is much evidence in the literature [5,7] for the former step being rate limiting in propene oxidation over molybdates and antimonates, in this case the response modes will not be conclusive as to whether the abstraction of the second hydrogen atom occurs before or after the insertion of oxygen.

Fig. 2b shows the responses when the second hydrogen abstraction is rate determining. The response of propene is drawn out due to a relatively large amount can adsorb, since a surface reaction step is rate limiting. The instantaneous part of the response is lower than in Fig. 2a, 2c and 2d and is due to the adsorption constant being larger (Table 3). During the first few minutes there is a build-up in the concentrations of $CH_2 = CH - CH_2O \cdot$ and $OH \cdot CH_2 = CH - CH_2O \cdot$ species then starts to decrease, explaining the small overshoots in the responses of acrolein and water. At the same time the surface coverage of propene and the allylic intermediate increase. Due to the lack of atomic oxygen, the coverage of adsorbed propene becomes larger than that of the allylic intermediate. At stationary conditions, the coverages of the two species must be the same (k_7 is equal to k_9 and the backward reactions are negligible) and consequently the coverage of propene has to start decreasing. Therefore, the response of propene has a small overshoot.

When the desorption of acrolein is rate determining, the responses become as shown in Fig. 2c. The response of propene can be explained as in previous examples. The response of water is almost instantaneous, since the rate limiting step does initially not affect the rate of water formation. During the first minutes there is large consumption of oxygen and the pressure of oxygen decreases. Since adsorbed acrolein blocks the oxygen sites, the pressure of oxygen finally increases. The blockage also makes the pressure of acrolein passing through a small maximum and the pressure of water a small minimum.

When the desorption of water is rate determining (see Fig. 2d), the responses can be explained as in the previous case, however, it should be observed that the response modes of acrolein and water show interchanged behaviour.

3.3. *Oxidation of propene to acrolein and carbon monoxide*

The reactions in Scheme 1 are now supplemented with the reactions in Scheme 3, showing

Table 3
Non default values [a] of the rate constants [b] that were used for the responses in Fig. 2

Rate determining step	Rate constants with non default values	
Second	$k_3 = 1 \cdot 10^{-3}$	$k_1, k_5, k_7, k_9, k_{11}, k_{13}, k_{15} = 1 \cdot 10^{-2}$
Sixth	$k_{11} = 1 \cdot 10^{-4}$	
Seventh	$k_{13} = 1 \cdot 10^{-5}$	$k_1, k_3, k_5, k_7, k_9, k_{11}, k_{15} = 1 \cdot 10^{-2}$
Eighth	$k_{15} = 1 \cdot 10^{-5}$	$k_1, k_3, k_5, k_7, k_9, k_{11}, k_{13} = 1 \cdot 10^{-2}$

[a] Default values: forward rate constants $1 \cdot 10^{-1}$, and backward rate constants $1 \cdot 10^{-9}$.

[b] The units of the rate constants are in accordance with the units in Table 1.

$$CH_2=CH-CH_3\,(g) + *' \xrightarrow{k_{17}} CH_2=CH-CH_3*'$$

Ninth step

$$O_2\,(g) + \bullet' \xrightarrow{k_{18}} O_2\bullet' \qquad O_2\bullet' + \bullet' \xrightarrow{k_{19}} 2\,O\bullet'$$

Tenth step Eleventh step

$$CH_2=CH-CH_3*' + O\bullet' \xrightarrow{k_{20}} I_1\bullet' + *' \qquad I_1\bullet' + O\bullet' \xrightarrow{k_{21}} I_2\bullet' + H_2O\bullet'$$

Twelfth step Thirteenth step

$$I_2\bullet' + O\bullet' \xrightarrow{k_{22}} I_3\bullet' + CO\bullet' \qquad I_3\bullet' + O\bullet' \xrightarrow{k_{23}} I_4\bullet' + H_2O\bullet'$$

Fourteenth step Fifteenth step

$$I_4\bullet' + O\bullet' \xrightarrow{k_{24}} I_5\bullet' + CO\bullet' \qquad I_5\bullet' + O\bullet' \xrightarrow{k_{25}} H_2O\bullet' + CO\bullet'$$

Sixteenth step Seventeenth step

$$CO\bullet' \xrightarrow{k_{26}} CO\,(g) + \bullet' \qquad H_2O\bullet' \xrightarrow{k_{27}} H_2O\,(g) + \bullet'$$

Eighteenth step Nineteenth step

Scheme 3. Mechanism for combustion.

a hypothetical mechanism for the combustion of propene to form CO over a series of intermediates (I_1–I_5). The model is consistent with the formation of acrolein and CO occur either on different crystal planes, or on the same plane but involve different adsorption and oxygen sites. Combustion mechanisms are not known in great detail but are believed to involve an attack by electrophilic oxygen on a double bond [8]. The reason for treating CO and not CO_2 in the

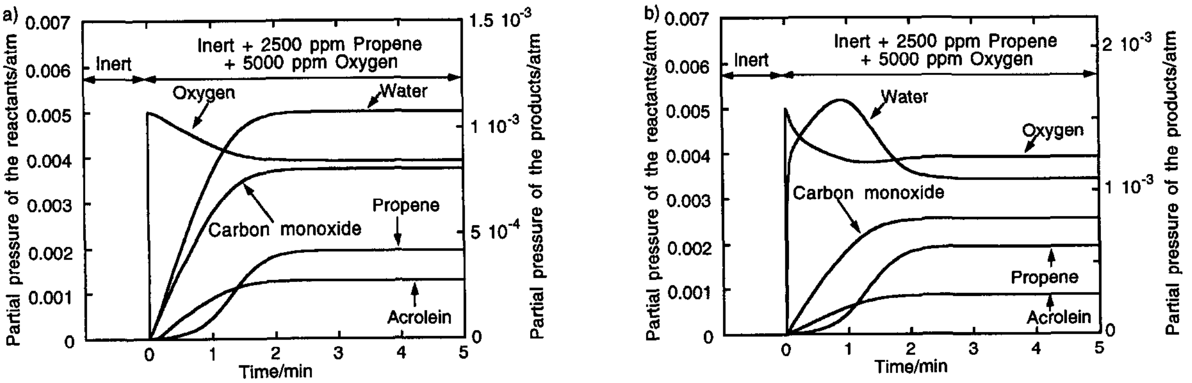


Fig. 3. Responses of reactants and products when the rate limiting steps are as follows: (a) fourth step ($k_7 = 1 \cdot 10^{-5}$) in the formation of acrolein and twelfth step ($k_{20} = 1 \cdot 10^{-5}$) in the formation of carbon monoxide; and (b) sixth step ($k_{11} = 1 \cdot 10^{-5}$) in the formation of acrolein and twelfth step ($k_{20} = 1 \cdot 10^{-5}$) in the formation of carbon monoxide. The forward rate constants are $1 \cdot 10^{-1}$ and the backward rate constants are $1 \cdot 10^{-9}$ with the exceptions given above. The oxygen sites are initially fully covered.

model calculations is to limit the number of reaction steps. However, this does not impose any restriction, since the considered examples concern combustion with the initial attack by oxygen as being rate limiting. Moreover, the simulations are performed for low conversion levels, corresponding to CO being an initial and not a consecutive product.

In Fig. 3 are the responses given to a step change from inert to inert with propene and oxygen for two sets of rate constants. Comparison of the responses in Fig. 3a with those in Fig. 1c suggests that the rate determining step in both acrolein and CO formation is a surface reaction, which is prior to water formation. In Fig. 3b, the initial response of water with a maximum and the minimum in the response of oxygen indicate that water is formed ahead of a rate limiting step, but whether this step is involved in the formation of acrolein, carbon monoxide or both is generally not possible to decide only from transient curves. The reason for the maximum of the water response is not so large in Fig. 3b as in Fig. 1d is due to the initial competition for gaseous propene between the two reaction pathways in the former case. It is, however, possible to distinguish contributions to the response from both pathways. The drawn out responses of acrolein and CO agree with a surface reaction is rate determining for the formation of each product.

4. Conclusions

Using propene oxidation as a model reaction, simulations were carried out of the transient responses of reactants and products to a step change from inert to reactant feed. Considering the response modes, which were calculated for various types of mechanisms, some conclusions of general significance for hydrocarbon oxidation over metal oxides can be formulated as follows:

(i) If the response of the reacting hydrocarbon is instantaneous and those of the products are steep, then the adsorption of the reactant is rate limiting.

(ii) When the oxygen sites are initially fully occupied, the oxygen response is always instantaneous.

(iii) When the adsorption of oxygen is rate limiting, the responses of the products are steep and each response pass through a maximum.

(iv) When a product is formed either in a rate limiting surface reaction step, or a succeeding step, the transient response shows a comparatively drawn out increase in pressure with time.

(v) When a product is formed in a step which is prior to the rate limiting step, the corresponding response is steep with a maximum.

(vi) Complex transient behaviour will appear when several steps affect the reaction rate.

The present results have demonstrated that a few transient experiments at an early stage of a mechanistic study can serve to reduce the number of mechanistic models that deserve further attention. However, conclusive results are not always obtained considering response shape only, since different types of mechanism can produce transients with identical feature. In such a case detailed mathematical analysis of kinetic parameters, or complementary investigation with other techniques may be necessary. The present work has concerned transients due to a step change from inert to inert with a complete set of reactants. Moreover, transient experiments with a step change from reactant gas to inert gas, as well as a step change in the concentration of one reactant can give additional information about the reaction mechanism.

In the calculations, the variation in surface coverage with oxygen was accounted for. However, responses can be affected also by restructuring of the oxide surface, e.g., phase change. This is not easily accounted for in model calculations.

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