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# A TAP reactor investigation of the oxidative dehydrogenation of propane over a V–Mg–O catalyst

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## Abstract

The oxidative dehydrogenation of propane (ODHP) was studied over an optimised V–Mg–O catalyst at 500°C using the vacuum transient kinetic technique in the temporal-analysis-of-products (TAP) reactor. The only products detected were $C_3H_6$ and $CO_x$. The experiments reveal that both, propene and carbon oxides are primary reaction products and that $CO_x$ is also produced by secondary oxidation of propene. Partial and deep oxidation of propane occur at the same surface site but involve different forms of reactive oxygen, associated to different site arrangements: nucleophilic lattice oxygen takes part in the propane partial oxidation to propene, while adsorbed electrophilic oxygen adspecies, originating from the gas-phase oxygen, are involved in the direct deep oxidation process of propane. The secondary oxidation of propene could involve both types of oxygen species. In the absence of gas-phase oxygen, the oxidation state of the catalyst determines the importance of the consecutive propene total oxidation. © 1998 Elsevier Science B.V.

## 1. Introduction

A kinetic investigation of the oxidative dehydrogenation of propane (ODHP) has been carried out by various research groups [1–8]. Most authors exclusively considered a consecutive reaction scheme, where $CO_x$ is only formed from the further oxidation of propene [1–6]. Studies reporting a more detailed reaction scheme are less numerous [7]. In fact, it is generally observed that the propene selectivity decreases with propane conversion and both selective and non-selective products are always observed even at low conversion levels [8]. Therefore, it is difficult to discriminate between a parallel and a sequential scheme for the partial/deep oxidation of propane.

In a recent study [8], the mechanism of the ODHP reaction over an optimised V–Mg-O catalyst was investigated by means of kinetic experiments combined with in situ FT–IR and steady-state isotopic transient kinetics (SSITK). Both, propene and carbon oxides were found to be primary reaction products. Thus, a purely consecutive scheme was ruled out and a parallel reaction scheme was proposed assuming a non-competitive activation of propane on two distinct types of sites (selective and non-selective). However, the SSITK analysis could not give any information about the occurrence of other steps such as the consecutive oxidation of propene into carbon oxides, possibly due to the limitation of the technique in time resolution (≈1 s time resolution).

The temporal-analysis-of-products (TAP) reactor is designed to operate in the transient mode in the millisecond time range, thereby largely improving

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the time resolution of the SSITK technique [9]. In this work, we used this technique in order to complete our mechanistic proposal focusing at investigating the role of oxygen in the above-mentioned key steps of the ODHP reaction.

## 2. Experimental

### 2.1. Catalyst preparation

A V–Mg–O catalyst containing 14 wt% V (referenced in the text as 14V/VMgO) was prepared by impregnation. The appropriate amount of the $Mg(OH)_2$ was added to a hot aqueous solution of ammonium metavanadate containing 1 vol% of $NH_4OH$. The suspension was evaporated to dryness and then dried overnight at 120°C. The resulting solid was crushed and calcined at 800°C under an $O_2$/He flow. The highest propene yield was obtained among a series of samples prepared with variable V contents with this catalyst [8,10,11].

### 2.2. Vacuum transient experiments

Vacuum transient experiments were carried out in the TAP reactor. A detailed description of the equipment is given elsewhere [9]. Therefore, only the specific conditions used in the present work are outlined below.

Two types of experiments were carried out:

(i) admission of single pulses onto the catalyst (16 experiments were averaged in order to increase the signal-to-noise ratio); and
(ii) sequential pulsing of two different substances from two different pulse valves onto the catalyst with a user-specified time difference $\Delta t$ (16 experiments were averaged in order to increase the signal-to-noise ratio).

The following gas mixtures were applied: $C_3H_8 : Ne=1 : 1$; $C_3H_8 : {}^{16}O_2 : Ne=1 : 2 : 6$; ${}^{18}O_2 : He=1 : 3$; $C_3H_8 : C_3H_6 : {}^{16}O_2 : Ne=2 : 1 : 1 : 6$; and $C_3H_6 : Ne=1 : 3$. Different pulse sizes were used in the experiments, amounting from $1\times10^{15}$ to $1\times10^{16}$ molecules per pulse. Additionally, long-term multi-pulses were performed for conditioning (oxidation, reduction) of the catalyst.

The response signals to the gas pulses at the reactor outlet were recorded by a quadrupole mass spectrometer and smoothed using a Fourier Transform method. Quantification of the results, i.e. calculation of conversions, selectivities and yields, was performed using Ne and He as internal standards. Fragmentation patterns of the pure substances and their sensitivities relative to the standards were recorded separately in a reactor filled with quartz particles ($d_P$=250–355 μm). Decomposition of the response signals at a specific *m/e* ratio was performed for the case of overlap of different substances.

In each experiment, 120 to 150 mg of the ex situ calcined catalyst ($d_P$=200–300 μm) was placed in the micro-reactor made of steel (bed height 9 mm) between two layers of quartz (bed height 10 mm). The temperature of the bed ($T_B$) was measured by a Ni–Cr–Ni thermocouple placed in the centre of the catalyst bed. The experiments were performed at $T_B$=495(±10)°C. The catalyst was heated to this temperature in vacuum at a rate of 25 K/min.

## 3. Results and discussion

### 3.1. Propane activation and product formation

A low-intensity propane single pulse was admitted onto the catalyst at 500°C in the absence (Fig. 1(a)) and presence (Fig. 1(b)) of oxygen. For these experiments, propane conversion was 21% in the absence and 32% in the presence of oxygen, while the oxygen conversion was 49%. The mean residence time of the non-converted propane on the surface, calculated from these experiments after correction for Knudsen diffusion, was ca. 1 ms, which corresponds to the limit of the TAP time resolution. Note that although no straightforward physical meaning can be attributed to the mean residence time calculated under reaction conditions, the occurrence of a significant accumulation of reversible propane on the catalytic surface can be discarded.

The only products detected at the reactor outlet as measurable pulses were propene, carbon monoxide and carbon dioxide. Water was trapped along the lines and no quantitative evaluation was attempted. Fig. 2 gives the $C_3H_6$, CO and $CO_2$ responses for the experiments described in Fig. 1. The mean residence time of

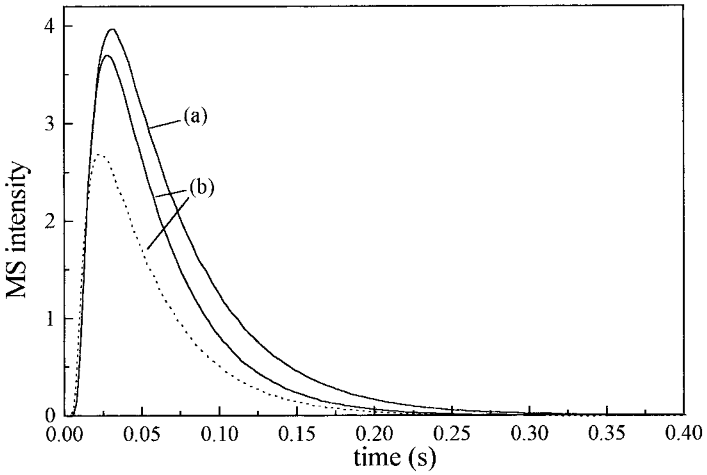

Fig. 1. Response signals of masses 29 ($C_3H_8$ ———) and 20 (Neon - - -) to a single pulse of (a) $C_3H_8$/Ne ($X_{C_3H_8} = 21\%$) and (b) $C_3H_8/O_2$/Ne ($X_{C_3H_8} = 32\%$) at $T_B$=495°C; $m_{cat}$=141 mg.

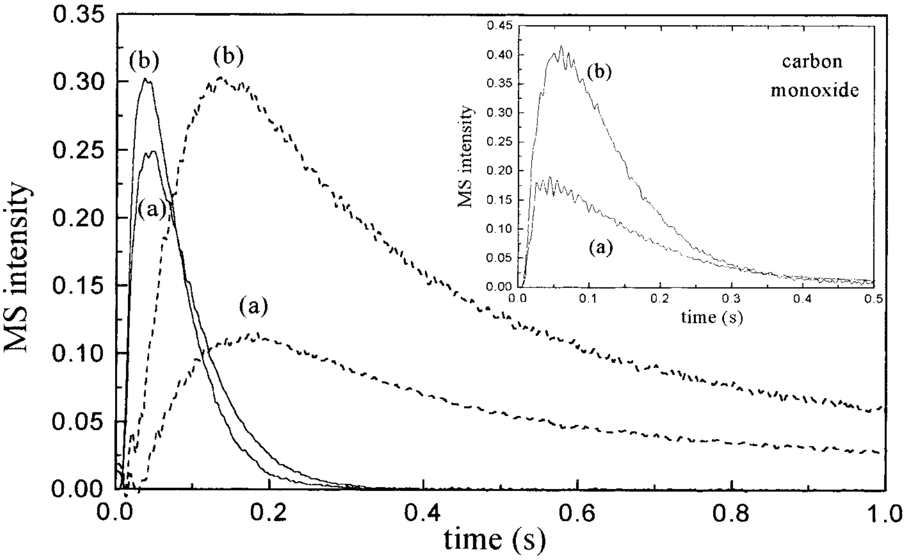

Fig. 2. Response signals of masses 41 ($C_3H_6$ ———) and 44 ($CO_2$ - - -) to a single pulse of (a) $C_3H_8$/Ne ($S_{C_3H_6} = 58\%$) and (b) $C_3H_8/O_2$/Ne ($S_{C_3H_6} = 38\%$) at $T_B$=495°C (see Fig. 1); $m_{cat}$=141 mg.

propene, calculated from these experiments, was close to that of propane ($\tau$=0.001 s), i.e. close to the limit of the TAP time resolution. However, the mean residence time of carbon oxide was estimated (a) at $\tau$=0.147 s for the $C_3H_8$/Ne pulse and (b) at $\tau$=0.286 s for the $C_3H_8/O_2$/Ne pulse. The foregoing values for the mean residence time of $CO_2$ indicated a strong interaction of $CO_2$ or its precursor with the catalyst surface. This could be related to (i) a slow process of oxidation involving, e.g. elementary steps, such as propoxy/carboxylate intermediates formation and decomposition, and/or (ii) a chromatographic effect due to adsorption/desorption phenomena occurring between the gaseous $CO_2$ and the basic surface sites through the catalyst bed, in accordance with the carbonate formation observed by in situ FT–IR [8]. The mean residence-time values were not calculated for CO responses, due to large uncertainties originating from mass overlapping. It can be observed, however, that the CO responses also present a curve tailing, but at a much lesser extent than the $CO_2$ responses. This could indicate that CO is formed through a shorter process than $CO_2$, as expected from a sequential route of total oxidation, where CO is first formed and thereafter further oxidised into $CO_2$.

The formation of both, $C_3H_6$ and $CO_x$ was observed in the absence of gaseous oxygen. However, propene selectivity decreased from 58 to 38% in the presence of gaseous oxygen (Fig. 2). This drop corresponded to an increase in propane conversion from 21 to 32% (Fig. 1). Thus, the propene yield was found to be practically similar in the presence or in the absence of oxygen (ca. 12%). This observation demonstrates that the ODHP is essentially controlled by a redox process, lattice oxygen being mainly involved in the selective pathway (favoured in the absence of gaseous oxygen) [8].

### *3.2. Nature and role of oxygen species*

The oxygen activation was also studied in the TAP reactor. A sample of 140 mg fresh catalyst (i.e. after ex situ calcination at 800°C under $^{16}O_2$/He flow) was loaded into the TAP reactor. The catalyst was reduced in situ under $C_3H_8$/Ne multi-pulses (1200 high-intensity pulses). It was then reoxidised in situ under $^{18}O_2$/He multi-pulses (2350 low-intensity pulses). After this pretreatment, a single pulse of propane (Fig. 3(A)) was admitted: pulses of $C_3H_6$, $C^{16}O$ (not reported here) and of $C^{16}O_2$ only were observed at the reactor outlet.

Further, alternating pulses of propane and labelled oxygen (Fig. 3(B)) were admitted at a time interval of 0.1 s. The formation rate of propene slightly decreased as compared to the previous experiment, whereas the $CO_2$ production was strongly enhanced in the presence of gaseous oxygen. The propene peak was observed simultaneously to the peak of propane, just as in the previous case. However, a faster decrease of the peak occurred when the oxygen pulse was admitted. The unlabelled and labelled $CO_2$ was essentially formed during the oxygen pulse, though a long tailing of the response signals indicated a residual production of $CO_2$ after the oxygen pulse (note that the apparent absence of $CO_2$ production at the very beginning of the propane pulse in Fig. 3(B) is an artefact coming from the defragmentation and smoothing calculation). $C^{16}O_2$ was essentially detected at the reactor outlet with some traces of $C^{18}O_2$ and $C^{16}O^{18}O$ ($[C^{16}O_2] : [C^{16}O^{18}O] : [C^{18}O_2]=42 : 4.2 : 1$). In contrast, neither $^{16}O_2$ nor $^{16}O^{18}O$ was detected among the unconverted oxygen.

Important mechanistic features can be derived from these experiments:

(i) The faster decrease of the propene outlet flux during the oxygen pulse (Fig. 3(B)) indicates that propene (or propene precursors) formed from the propane pulse can be further oxidised into carbon oxide species with gaseous oxygen (or more likely

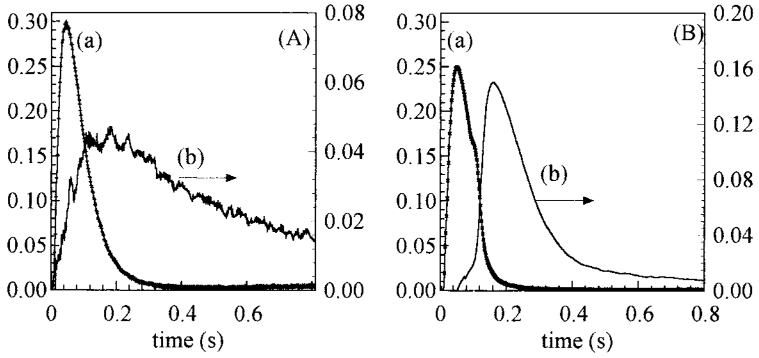

Fig. 3. Response signals of masses (a) 41 ($C_3H_6$ –+–) and (b) 44 ($C^{16}O_2$ ––) to (A) single pulse of $C_3H_8$/Ne ($X_{C_3H_8} = 30\%, S_{C_3H_6} = 84\%$) and (B) alternating pulses of $C_3H_8$/Ne and $^{18}O_2$/He ($X_{C_3H_8} = 29\%, S_{C_3H_6} = 70\%$) at $T_B$=495°C; $m_{cat}$=141 mg.

from activated oxygen species directly issued from the reaction of gaseous oxygen with the catalytic surface). Some of these activated oxygen species could be stable enough to remain on the catalyst and to react with the propene formed from the propane pulse. This would explain the slight decrease in the propene pulse height in comparison with the propene pulse observed in the absence of oxygen pulse (Fig. 3(A)). As already discussed, the long tailing of the $CO_2$'s response signals could originate either from these residual oxygen ad-species reacting slowly with carbonaceous residues or from the slow decomposition of the carbonate pool occurring under vacuum conditions.

(ii) A quasi-exclusive formation of $C^{16}O_2$ was observed for both experiments. A first explanation is that the $^{18}O$ atoms which were consumed by the reduced catalyst for regenerating/reoxidising the active sites were completely mixed into a very large 'reservoir' of $^{16}O$ atoms (lattice oxygen). This almost suppressed the probability of having active labelled oxygen on the surface available for total oxidation. A second explanation is that once formed, the $CO_2$ molecules underwent a fast isotopic exchange with the lattice oxygen along the catalytic bed through the above-mentioned chromatographic effect. Whatever be the exact origin of the observed phenomenon, it can be concluded that a fast diffusion of oxygen atoms throughout the oxide occurred under the reaction conditions.

(iii) No $^{16}O_2/^{18}O_2$ isotopic scrambling was observed along the oxygen pulse. Since the occurrence of oxygen exchange implies both a reversible dissociation and a fast lattice oxygen diffusion, it can be deduced from the previous statement than no reversible activation of oxygen occurred under the prevailing conditions.

### 3.3. State of the active surface and propene selectivity

A sample of 127 mg fresh catalyst (i.e. after ex situ calcination at 800°C under an $^{16}O_2$/He flow) were loaded into the TAP reactor. The catalyst was progressively treated in situ under $C_3H_8$/Ne multi-pulses (900 high-intensity pulses), aiming at suppressing surstoichiometric, then stoichiometric oxygen atoms from surface and bulk. Conversion and product selectivities were calculated at the end of each set of multi-pulses. The results are reported in Table 1.

Table 1
Changes in conversion and product selectivities during high-intensity single pulses of propane, $m_{cat}$=127 mg, at $T_B$=495°C, after successive in situ reductions by $C_3H_8$/Ne multi-pulsing

| $C_3H_8$/Ne multi-pulses | $X_{C_3H_8}$ (%) | $S_{C_3H_6}$ (%) | $S_{CO_x}$ (%) |
|---|---|---|---|
| 0 pulses | 26 | 54 | 46 |
| 900 pulses | 13 | 92 | 8 |
| 1800 pulses | 11 | 97 | 3 |
| 2700 pulses | 10 | 100 [a] | 0 |
| 3600 pulses | 14 | 100 [a] | 0 |
| 4500 pulses | 11 | 100 [a] | 0 |

[a] Only traces of $CO_x$.

As seen in Table 1, a drop in propane conversion (from 26 to 13%) was observed after the first set of propane multi-pulses, and was followed by an increase in propene selectivity (from 54 to 92%). Thereafter, the propane conversion level tended to stabilise while the selectivity to propene reached 100%. Initial activity and selectivity were completely recovered after catalyst reoxidation.

Again, important features can be derived from these experiments:

(i) $CO_x$ are mostly formed from activated oxygen species, which exist only on freshly oxidised material and disappear after surface oxygen depletion. In that sense, the non-selective pathway would be related to the presence of vanadium ions in their highest oxidation state, i.e. $V^{5+}$ ions.

(ii) It is confirmed that propene is formed via a redox process involving lattice oxygen since only propene is produced on a sample depleted in surstoichiometric oxygen. If one admits that several oxidation states of vanadium coexist under reaction conditions (see XPS and EPR measurements reported in [8]), this could mean that the selective propane activation involves more $V^{4+}$ and $V^{3+}$ ions rather than $V^{5+}$.

The stabilisation of propene production after a large number of propane pulses is surprising. It could suggest that the rate of surface reoxidation via lattice oxygen migration from the bulk is fast enough to maintain a steady oxidation state of the active surface after the propane pulses. Another explanation is that only a part of the catalytic bed is deactivated after a series of propane pulses and that the remaining part continues to be active and to produce propene. This would correspond to the progressive displacement of a deactivation front along the bed. Whatever be the explanation, it can be forecast that a complete deactivation of the solid should be reached after pulsing the adequate amount of propane. A similar effect of progressive but complete deactivation was observed by treating the catalyst under pure flowing propane at atmospheric pressure [10].

(iii) The process of catalyst reduction is completely reversible, in agreement with in situ electrical conductivity measurements reported in [8,11].

### 3.4. Propene addition to the feed

In order to investigate whether $CO_x$ products are also formed through propene oxidation, $C_3H_6$ was added to the feed (10.5 vol%). The responses of propane, oxygen and $CO_2$ are shown in Fig. 4. The addition of propene in the feed induced (i) a drop in propane conversion (from 37 to 18%), (ii) a decrease in the amount of $CO_2$ formed (Fig. 4(B)), and (iii) no effect in oxygen conversion. The propene conversion was 55%. Thus, the addition of propene in the feed appeared to inhibit the ODHP reaction. The preferential adsorption of propene on acidic $V^{5+}$ sites via the $\pi$-bonding electrons, blocking the propane activation process, could explain this effect.

Low-intensity single pulses of $C_3H_6$/Ne were then admitted to the catalyst. For these experiments, the propene conversion was 58%, which is quite similar to the propene conversion under the $C_3H_8/C_3H_6/O_2$/Ne pulse ($X_{C_3H_6} = 55\%$). Thus, it was shown that propene itself could easily be oxidised to $CO_x$ in the absence of gaseous oxygen. This strongly confirms that a secondary non-selective route oxidising propene by means of residual surface activated oxygen and/or via lattice anion $O^{2-}$ occurs in competition with the selective activation of propane.

The changes induced on the catalyst by the treatment under an atmosphere of propene were studied by comparing the responses of a $C_3H_8/O_2$/Ne single pulse before, and after the series of propene pulses. A drop in propane conversion (from 37 to 22%) was observed after the $C_3H_6$/Ne pulses, whereas the oxygen conversion level remained approximately constant (49 to 50%). A decreased production of carbon dioxide was equally observed which corresponded to a considerable increase in the propene selectivity (from 35 to 81%).

These observations can be rationalised as follows: (i) a part of the active sites for propane activation was reduced/deactivated under propene atmosphere, and (ii) the gaseous oxygen further admitted on the reduced surface was mostly consumed for regenerating/reoxidising the reduced sites into selective sites, and not into non-selective sites leading to total oxidation. This fully agrees with a previous statement from this work that the non-selective sites can exist only on a reoxidised surface.

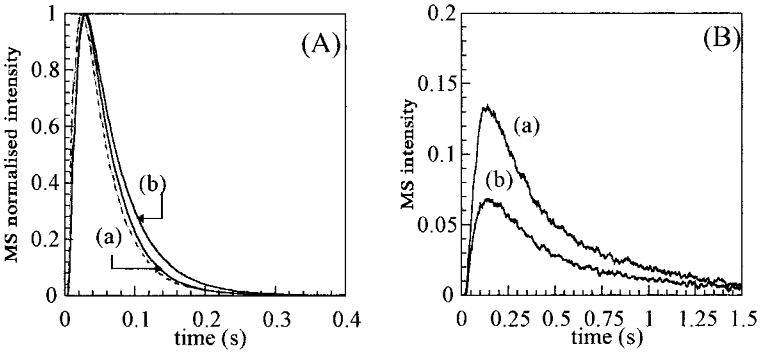

Fig. 4. Response signals of (A) masses 29 ($C_3H_8$ ———) and 20 (Neon - - -) and (B) mass 44 ($CO_2$ ———) to a single pulse of (a) $C_3H_8/O_2$/Ne ($X_{C_3H_8} = 37\%$) and (b) $C_3H_8/C_3H_6/O_2$/Ne ($X_{C_3H_8} = 18\%$) on fresh catalyst at $T_B$=495°C; $m_{cat}$=141 mg.

### 3.5. ODHP reaction network

It was shown from the propane single-pulse experiments (Fig. 2, Table 1) that propene could be formed from propane in the absence of gaseous oxygen, clearly demonstrating a Mars–van Krevelen mechanism via the reduction of an active site involving lattice oxygen species and probably vanadium ions in intermediate oxidation state. This site configuration corresponding to the selective propane-to-propene route will be referred to as $x_O$.

$CO_2$ was found to be produced in the absence of gaseous oxygen on a freshly oxidised catalyst but not on a partially reduced solid. In a consistent way, the $CO_x$ selectivity was found to decrease considerably on increasing the degree of reduction of the catalyst (Table 1). However, the formation rate of $CO_2$ was enhanced in the presence of gaseous oxygen, e.g. when sequentially, or better still simultaneously, pulsing propane and oxygen in the TAP reactor (Figs. 2 and 3). During multi-pulsing with propane, the activated oxygen species were consumed and the non-selective pathway suppressed. However, propene was still produced while consuming lattice oxygen. Kung et al. [12] observed a similar correlation between selectivity for dehydrogenation of butane over a $V_2O_5/\gamma$-$Al_2O_3$ catalyst and the degree of catalyst reduction.

It can thus be stated that the non-selective route for propane to $CO_x$ involves sites which exist only on a fully oxidised surface. Though no direct in situ characterisation of these sites has ever been reported, these sites are likely to involve highly active oxygen species such as the electrophilic $O^-$, $O_2^-$, $O_2^{2-}$ species and, accordingly, vanadium ions in their highest possible oxidation state, $V^{5+}$ [13]. Accordingly, these sites will be described as superoxidised forms, $x_{OO}$, of the oxidised sites $x_O$ defined above. The activation of propane on these nucleophilic non-selective sites would result in the formation of C–O bonds leading to propoxy intermediates, which could decompose stepwise to carboxylates and carbonates and, finally, desorb as combustion products. The complexity of the overall process is reflected by the relatively long residence time of $CO_2$ precursors measured in the TAP experiments.

A secondary route for $CO_x$ formation via propene oxidation was also revealed by the high reactivity of propene with the solid as a pure reactant, or added to the propane/oxygen feed:

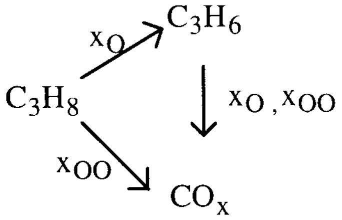

Fig. 5. The ODHP simplified reaction scheme.

- When admitted as a reactant in the absence of oxygen, propene was rapidly oxidised into $CO_x$, leading to a marked reduction of the solid.
- When propene was added in the feed pulse (Fig. 4), the propane conversion decreased significantly and the ODHP reaction was inhibited.

It may therefore be concluded that propene is activated in competition with propane to form combustion products. Both $x_O$ and $x_{OO}$ sites could be involved in this secondary process.

To summarise, the following simplified scheme (Fig. 5) depicts the main reaction pathways which occur during the ODHP process:

(i) a selective propane-to-propene route via the reduction of oxidised sites $x_O$;
(ii) a non-selective propane-to-$CO_x$ route via superoxidised sites $x_{OO}$; and
(iii) a non-selective propene-to-$CO_x$ route via oxidised sites $x_O$ and/or $x_{OO}$.

Indeed, the steps dealing with the regeneration of the reduced sites have to be considered in a complete mechanistic scheme. It also has to be noted that another secondary route, such as the CO-to-$CO_2$ pathway, has been omitted at this stage of the study since no clear indication was obtained from the present TAP experiments.

## 4. Conclusion

The ODHP reaction mechanism was studied over an optimised V–Mg–O catalyst by use of the TAP reactor. A Mars–van Krevelen reaction mechanism was proposed involving a fast oxygen migration through the oxide lattice. However, oxygen labelling showed no gaseous oxygen exchange, revealing that oxygen could only be consumed irreversibly by the solid (reoxidation, creation of activated oxygen species) but not reversibly dissociated (like on an metallic surface). As far as oxygen species are concerned, lattice oxygen would be involved in the formation of propene, while activated oxygen adspecies seemed to be related to the non-selective propane-to-$CO_x$ pathway. Indeed vanadium ions in various oxidation states and anionic vacancies have also to be considered to fully characterise the active sites [11].

The following mechanistic scheme was tentatively proposed:

– a unique active site is considered with three possible states: oxidised ($x_O$), reduced ($x$) and superoxidised ($x_{OO}$);
– the selective route leading to propene formation occurs on the oxidised site ($x_O$);
– a primary non-selective route oxidising propane into $CO_x$ involves the superoxidised sites ($x_{OO}$);
– a secondary non-selective route oxidising propene into $CO_x$ also occurs in competition with the selective activation of propane; and
– gaseous oxygen would either regenerate the reduced active sites or react with them to form non-selective adspecies ($x_{OO}$).

Further kinetic modelling is in progress on the basis of these mechanistic features.

## Acknowledgements

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## References

[1] M.A. Chaar, D. Patel, H.H. Kung, J. Catal. 109 (1988) 463.
[2] N. Boisdron, A. Monnier, L. Jalowiecki-Duhamel, Y. Barbaux, J. Chem. Soc. Trans. 91(17) (1995) 2899.
[3] S.L.T. Anderson, Appl. Catal., A: General 112 (1994) 209.
[4] J. De Morais, Ph.D. thesis, University of Lyon (F), 1995.
[5] R.H.H. Smits, Ph.D. thesis, University of Twente (NL), 1994, ISBN 90-9006885-6.
[6] D. Creaser, B. Andersson, Appl. Catal., A: General 141 (1996) 131.
[7] J.N. Michaels, D.L. Stern, R.K. Grasselli, Catal. Lett. 42 (1996) 135.
[8] A. Pantazidis, C. Mirodatos, in J.W. Hightower, W.N. Deglass, E. Iglesia, A.T. Bell (Eds.), 11th International Congress on Catalysis – 40th Anniversary, Stud. Surf. Sci. and Catal. 101 (1996) 1029; ibidem, Heterogeneous Hydrocarbon Oxidation, in B.K. Warren, S.T. Oyama (Eds.), ACS Symposium Series, Washington, 638 (1996) 207–222.
[9] J.T. Gleaves, J.R. Ebner, T.C. Kuechler, Catal. Rev.-Sci. Eng. 30 (1988) 49.
[10] A. Pantazidis, Ph.D. thesis, University of Lyon (France), 1996.
[11] A. Pantazidis, A. Burrows, C. Geantet, C. Mirodatos, C.J Kiely, Catal. (1998) in press.
[12] H.H. Kung, P. Michalakos, L. Owens, M. Kung, P. Andersen, O. Owen, I. Jahan, Catalytic Selective Oxidation, in S.T. Oyama, J.W. Hightower (Eds.), ACS Symposium Series 523 (1992) 389.
[13] A. Bielanski, J. Haber, Catal. Rev.-Sci. Eng. 19 (1979) 1.