Oxygen exchange at Mo/V mixed oxides
A transient and ^{18}O isotope study under technical conditions

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Abstract

Mo/V mixed oxides have proven themselves to be reliable for the partial oxidation of acrolein to acrylic acid. Methacrolein which is the homologue of acrolein, reacts with clearly worse selectivity and activity on this catalyst system. By means of transient investigations (TP reduction, CP reduction, CP reaction and ^{18}O-SSITKA) under reaction conditions, it was possible to provide a contribution towards clarifying the oxygen exchange of the Mo/V mixed oxides during the reaction of both aldehydes to the corresponding carboxylic acids. In the case of both aldehydes, an exchange of carbonyl oxygen and solid oxygen occurs on the Mo/V mixed oxide. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Transition metal oxides have proven themselves to be reliable as catalysts for heterogeneous catalysed partial oxidations [1]. They were introduced for this reason for the two-stage acrylic acid production from propene via acrolein, in this particular example as Bi/Mo (first stage) and also Mo/V mixed oxides (second stage) [2,3]. Because of the multi-functionality of mixed oxides, there is a great interest in the clarification of the kinetic, mechanistic and structural properties of this system based on a rational catalyst design [4,5]. It was possible to identify the catalytic active phase of the Bi/Mo mixed oxide in propylene oxidation to acrolein [6] and also to explain the reaction mechanism of that particular reaction [7,8].

At present, the image of the Mo/V mixed oxides is still unclear. An allocation of structural properties to the kinetic data, proves to be difficult, because the addition of promoters (Cu, Fe, W among others [3]) gives rise to a significant increase in the number of possible phases. Tichy et al. [9] identified VMo_3O_{11} as an active phase in model catalysts. Werner et al. [10] specify Mo_4VO_{14} as an active phase. In both cases they relate to strongly disordered layered structures, which belong to the class of shear structures that are capable of providing or incorporating oxygen reversibly by a shearing of the structure. Werner et al. postulate an additional mechanism for the reversible incorporation and removal of oxygen, in which small regions of corner-sharing octahedrons restructure to edge-sharing octahedrons, setting free oxygen. They show that this mechanism

is energetically more favourable than wide area shearing.

The reason for the good catalytic property appears to be, among various other reasons, that no well-crystallised phases are present here, phases with a high portion of X-ray amorphous structures can be found instead [11]. These can be obtained by means of spray drying a catalyst precursor solution.

Andrushkevich states that Mo/V mixed oxides, acrolein and higher homologues all react according to the same mechanism to form carboxylic acids [12]. Shimizu et al. [13] and our own work [11] show that methacrolein reacts with a poorer activity/selectivity behaviour to form methacrylic acid than acrolein does forming acrylic acid. Up to now, no satisfactory explanation for this could be found.

In this work with the help of transient methods and [18]O isotope experiments under technical conditions, the behaviour of acrolein and methacrolein on a partly X-ray-amorphous Mo/V mixed oxide was investigated.

2. Experimental set-up

2.1. Catalyst

The specimen used relates to a mixed oxide with an overall composition $Mo_9V_2W_{1,2}O_x$ which was synthesised by thermal decomposition of the corresponding ammonium salts. The sample was in powder form with an average particle size of $80\,\mu m$ (BET surface area: $14\,m^2\,g^{-1}$). A detailed description and characterisation can be found in [3,15,17].

2.2. Apparatus

The measurements were carried out in a self-constructed micro-apparatus (Fig. 1) involving a fully automatic changing of temperature or concentration programme procedure, with different gas mixtures. A detailed description of the whole experimental set-up can be found in literature [11,14].
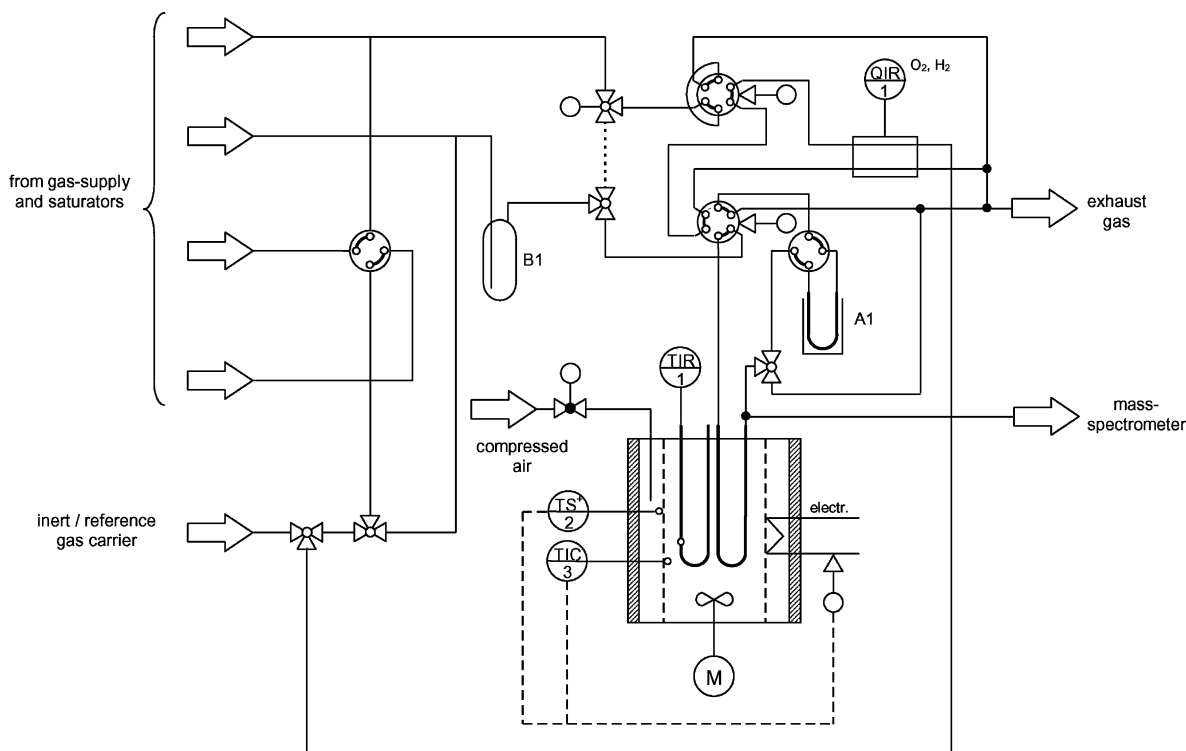

Fig. 1. Part of the flow sheet showing the measuring apparatus.

Table 1
Explanation of the experiments shown by type

No.	Method	Disturbance	Reactants (rest N_2)
1	TP reduction	Constant heating	5 vol.% aldehyde
2	CP reduction	Concentration jump	5 vol.% aldehyde
3	CP reaction	Concentration jump	5 vol.% aldehyde, 15 vol.% $^{18}O_2$
4	SSITKA (steady-state isotopic kinetic analysis)	Change of the oxygen isotope from $^{16}O_2$ to $^{18}O_2$	5 vol.% aldehyde, 15 vol.% $^{18}O_2$

2.3. Catalyst pre-treatment and experimental procedure

The investigations carried out can be divided into four methodical sections (Table 1).

Before commencing the experiments, the catalyst was pre-treated as follows: for methods 1–3, a conditioning took place with 10 vol.% oxygen in nitrogen at 300 °C for 1 h. This was followed by flushing out the reactor with nitrogen. For method 4, the specimen was treated for 3 h with a reaction mixture of 5 vol.% of aldehyde and 15 vol.% $^{16}O_2$ in nitrogen at 300 °C. This was followed by flushing out the reactor with nitrogen. Subsequently, the actual measurements were carried out. This meant that in the case of the TP reduction, a constant educt stream was adjusted and the specimen was heated at a constant rate. In the case of the CP reduction, the oven temperature was held constant and an educt concentration jump was carried out. In the case of method 4, the flushing out with nitrogen was omitted. With a constant aldehyde stream, there was a direct switch from $^{16}O_2$ to $^{18}O_2$ (see also Fig. 2). This so called "steady-state isotopic transient kinetic analysis" (SSITKA) guarantees that the observed results can be obtained under real conditions, i.e. with the actual operating catalyst, the corresponding gas concentrations, pressures and temperatures. The experimental challenge consists of not only maintaining the educt-concentrations (aldehyde and oxygen) and the flow rate at constant values, during the change-over procedure from $^{16}O_2$ to $^{18}O_2$, but also of avoiding pressure surges. The concentration change of the reactants, which follows the exerted disturbance, was detected at the reactor outlet, by means of a quadrupol mass spectrometer.

3. Results and discussion

3.1. TP reduction

Fig. 3 shows that acrolein is converted into acrylic acid from 150 °C on upwards. The total oxidation products, CO_2 and H_2O, are detected at about 230 °C together with a simultaneous fall in the acrylic acid concentration. At about 430 °C, a more powerful
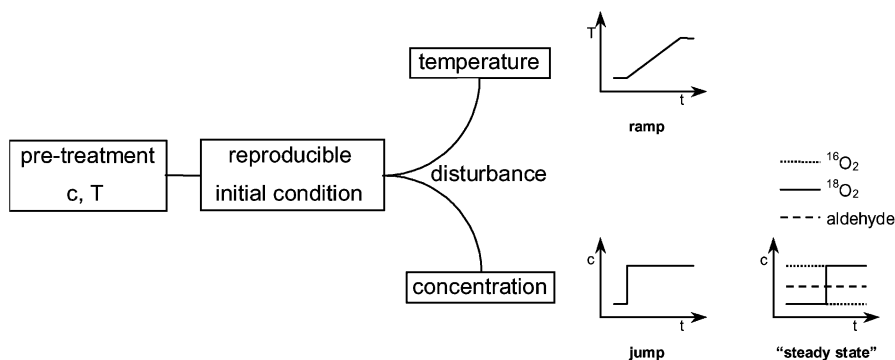

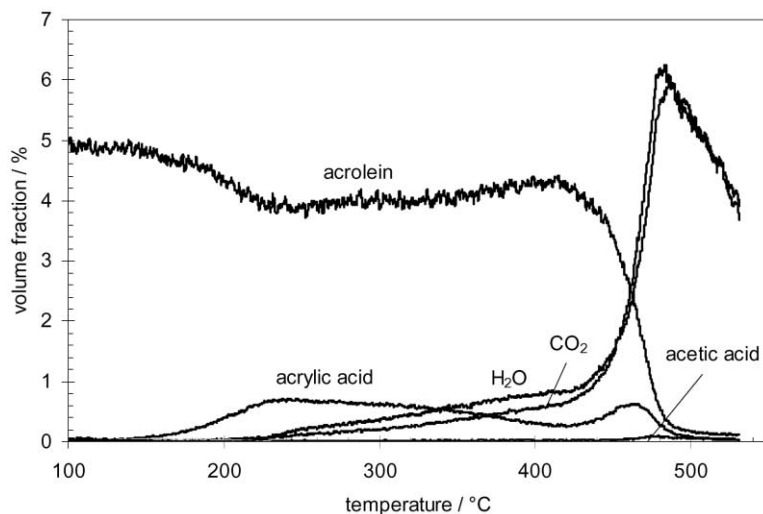Fig. 2. Transient methods shown by type of disturbance.

Fig. 3. TP reduction (acrolein), weight of sample 209 mg; volume-flow 20 ml min^{-1}; pre-treatment: 10 vol.% O_2 in N_2, 300 °C, 60 min; experimental conditions: heating rate 10 °C min^{-1}, 5 vol.% acrolein in N_2.

increase of CO_2 and H_2O can be recognised. This can be traced back to a change in the solid structure with the emission of lattice oxygen. However, this oxygen is not emitted into the gas phase, but results in the total oxidation of acrolein.

In the case of methacrolein (Fig. 4), methacrylic acid cannot be registered—only the total oxida-tion products (at about 170 and 200 °C). At about 430 °C, a great increase of combustion products can again be registered. The ratio of CO_2 to H_2O does not correspond to a theoretical total com-bustion. This means that during this procedure, the catalyst becomes covered with a layer of coke.
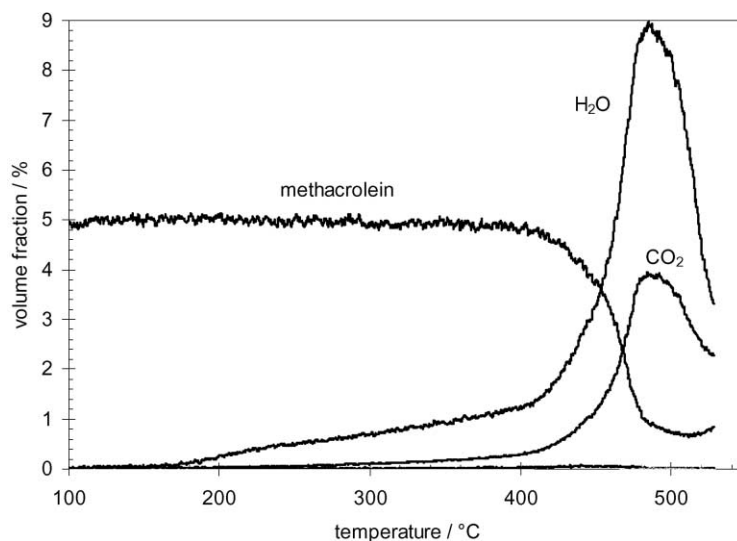

Fig. 4. TP reduction (methacrolein), weight of sample 209 mg; volume-flow 20 ml min^{-1}; pre-treatment: 10 vol.% O_2 in N_2, 300 °C, 60 min; experimental conditions: heating rate 10 °C min^{-1}, 5 vol.% methacrolein in N_2.

The TP reductions show the different behaviour of both of the test molecules: in contrast to acrolein, methacrolein is obviously not able to activate the oxygen of the catalyst selectively in the absence of gas phase oxygen. From TP desorption measurements it is known that methacrylic acid can desorb from the catalyst, i.e. it would be possible to detect any methacrylic acid that might be formed during TP reduction. With acrolein, in contrast, the reaction takes place at various active sites which have different selectivities with regard to acrylic acid [11,16].

3.2. CP reduction

From the CP reductions (Figs. 5 and 6), we can see, that the Mo/V mixed oxide is significantly more active toward acrolein compared with methacrolein. It was possible to detect a conversion showing a small amount of methacrylic acid, when introducing methacrolein as a probe molecule, only with higher catalyst masses.

The comparison of specific quantities of acid formed (acid formed per unit mass of catalyst) shows that acrolein can selectively activate substantially more catalyst oxygen to the corresponding acid than methacrolein.

Under the CP reduction conditions, a small amount of methacrylic acid can be detected. This can be described by the fact that the initial activity in the jumps lies somewhat higher than in the linear rise in temperatures with time. This is because the temperature history is missing in the jump experiments and because all the oxygen is still available, e.g. at 300 °C and that, in contrast, would already have been used up at this temperature in a TP reduction experiment.

3.3. CP reaction (jump: $^{18}O_2$ + aldehyde)

The main difference between the previous experiments and this method is the presence of oxygen in the gas phase during the reaction. Additionally an oxygen isotope has been used with regard to the oxygen incorporation. Fig. 7 shows a CP reaction experiment with acrolein and $^{18}O_2$ after a catalyst pre-treatment with $^{16}O_2$.

Two occurrences are obvious:

1. The appearance of the ^{18}O-containing acid immediately at the beginning of the jump indicates a fast re-oxidation mechanism of oxygen vacancies on the catalyst surface. The assumption up to now that the re-oxidation of the surface only takes place over the bulk has to be extended by the
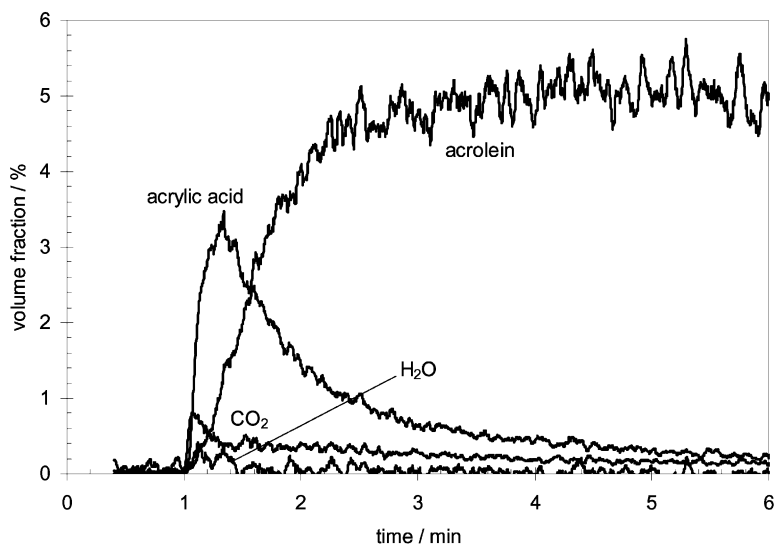

Fig. 5. CP reduction (acrolein), weight of sample 50 mg; volume-flow 20 ml min^{-1}; pre-treatment: 10 vol.% O_2 in N_2, 300 °C, 60 min; experimental conditions: temperature 320 °C, 5 vol.% acrolein in N_2.
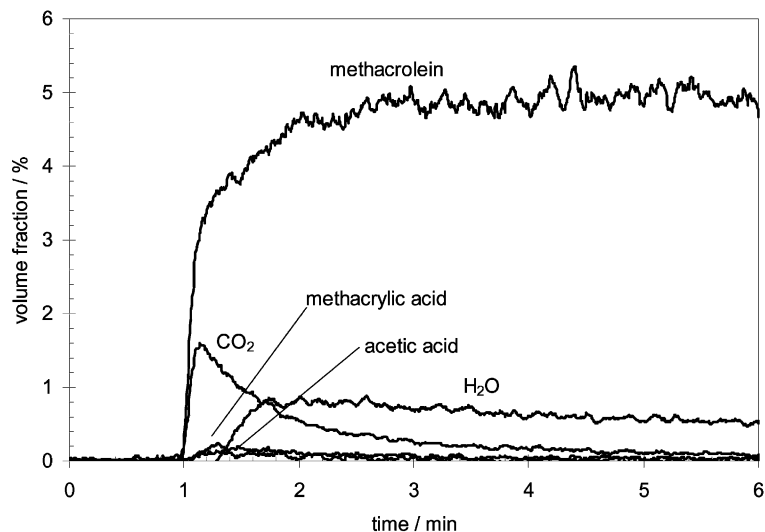
Fig. 6. CP reduction (methacrolein), weight of sample 210 mg; volume-flow 20 ml min^{-1}; pre-treatment: 10 vol.% O_2 in N_2, 300 °C, 60 min; experimental conditions: temperature 300 °C, 5 vol.% methacrolein in N_2.

possibility of re-oxidation through gas phase oxygen on the surface. But if the rate of bulk oxygen diffusion to the surface vacancies is in the same order as the surface reaction rate of oxygen with the aldehyde, the re-oxidation pathways are not distinguishable by analysis of the gaseous products Fig. 8.

A similar spectrum appears for methacrolein. Here ^{18}O can also be detected in the products starting at the very beginning of the jump. In contrast to the measurements in the absence of gas phase oxygen, the methacrylic acid selectivity is increased, probably based on a decrease in the observed coke layer described above.
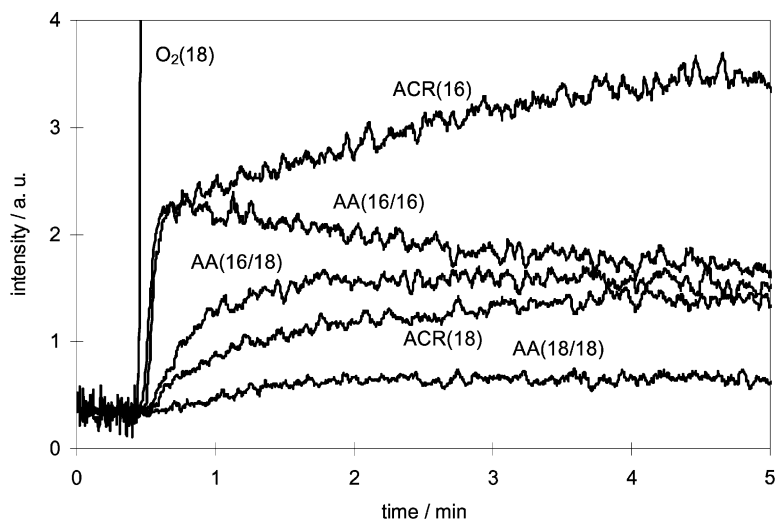

Fig. 7. CP reaction (acrolein + $^{18}O_2$) Weight of sample 26 mg; volume-flow 20 ml min^{-1}; pre-treatment: 10 vol.% $^{16}O_2$ in N_2, 300 °C, 60 min; experimental conditions: temperature 300 °C, 5 vol.% acrolein and 15 vol.% $^{18}O_2$ in N_2.

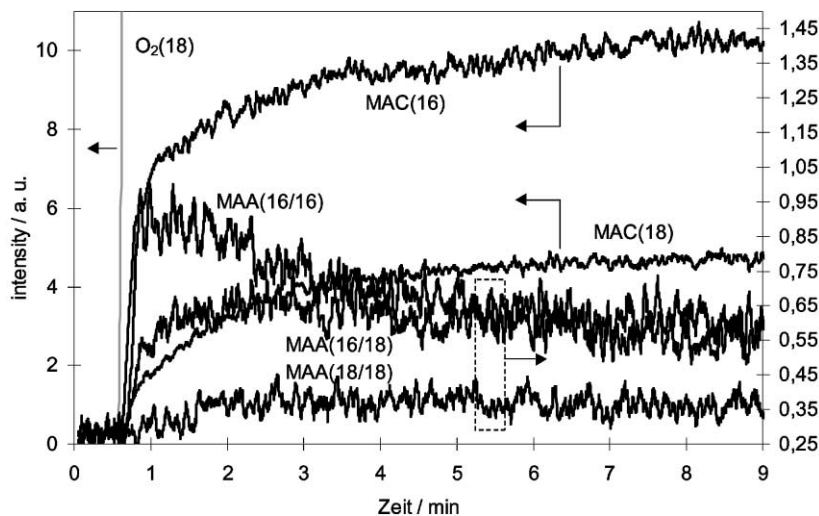Fig. 8. Weight of sample 203 mg; volume-flow 20 ml min^{-1}; pre-treatment: 10 vol.% $^{16}O_2$ in N_2, 300 °C, 60 min; experimental conditions: temperature 300 °C, 5 vol.% methacrolein and 15 vol.% $^{18}O_2$ in N_2.

2. As a further peculiarity it is shown that the carbonyl oxygen (R–CH$\underline{O}$) of both test-molecules, acrolein as well as methacrolein, is exchanged with oxygen of the re-oxidised catalyst (R–CH^{16}O + Mo$_9$V$_2$W$_{1,2}$$^{16}O_y$$^{18}O_z$ → R–CH^{18}O + Mo$_9$V$_2$-W$_{1,2}$$^{16}O_{y+1}$$^{18}O_{z-1}$). Subsequently the isotope exchanged aldehyde is desorbed again and undergoes further reaction, respectively. This also explains the detection of the double ^{18}O-labelled meth- and acrylic acid (MAA(18/18) and AA(18/18)). In this case, the aldehyde first exchanges its oxygen ^{16}O by ^{18}O on the catalyst surface, and then it reacts further to ^{18}O-labelled acid (R–CH^{18}O + Mo$_9$V$_2$W$_{1,2}$$^{16}O_y$$^{18}O_z$ → R–C$^{18}O$$^{18}OH$ + Mo$_9$V$_2$W$_{1,2}$$^{16}O_y$$^{18}O_{z-1}$) Fig. 9.

3.4. SSITKA

By means of the introduced experimental set-up, it was possible to study this in situ exchange procedure under steady-state conditions. Fig. 10 shows an example of acrolein with the oxygen isotope exchange, and the changes which result from the reaction.

Here, ^{18}O also appears in the products immediately after switching from $^{16}O_2$ to $^{18}O_2$. The sum of ^{16}O- and ^{18}O-labelled acrolein signals are constant as well

as the sum of the acrylic acid isotopes signals indicating steady-state conditions for the overall reaction during the isotope change. The decrease of the intensity of mass spectrometer signal corresponding to the ^{16}O-labelled acrolein is equal to the increase of the ^{18}O-labelled acrolein signal. Both signals converge to constant values due to a steady-state oxygen exchange with time. An ^{16}O-incorporation into the catalyst as a result of the oxygen exchange from the aldehyde is also indicated by the non-zero level of the (16/16) acrylic acid signal with time. So, the ^{16}O-content of the catalyst will not level off to zero, but to a constant value depending to the feed concentration
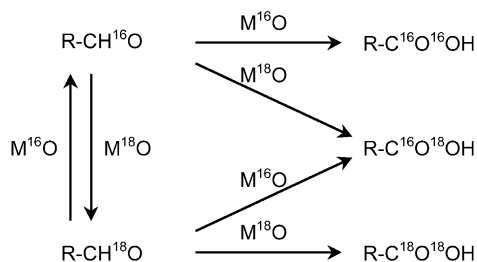

Fig. 9. Pathways of the isotopic exchange referring to the reaction of acrolein (R: CH$_2$CH) or methacrolein (R: CH$_2$CHCH$_3$) at a Mo/V mixed oxide catalyst which contains ^{16}O as well as ^{18}O.
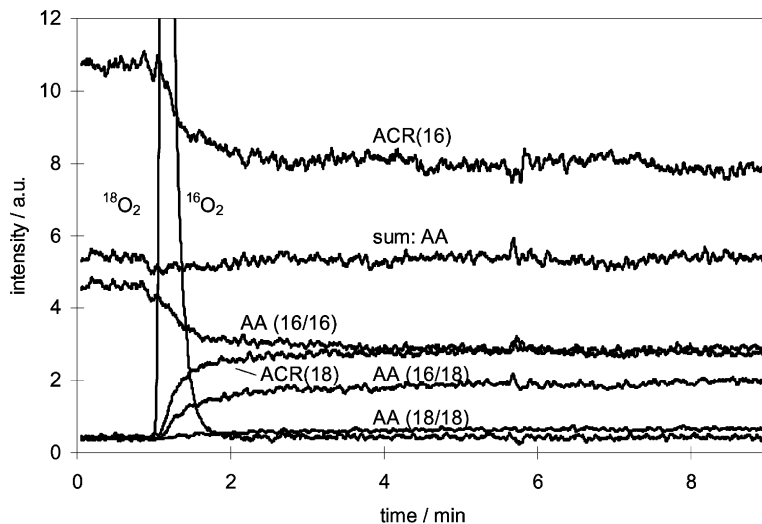
Fig. 10. Weight of sample 26 mg; volume-flow 20 ml min^{-1}; pre-treatment: 5 vol.% acrolein and 15 vol.% $^{16}O_2$ in N_2, 300 °C, 180 min; experimental conditions: temperature 300 °C, 5 vol.% acrolein and 15 vol.% $^{16}O_2$ or $^{18}O_2$ in N_2.

of the ^{16}O-containing acrolein at the reactor inlet Fig. 11.

A similar behaviour is found using methacrolein. Thus, the results confirm under reaction conditions, those obtained with the CP reactions, which is the rapid oxygen exchange and the exchange of carbonyl oxygen according to the scheme given in Fig. 9.
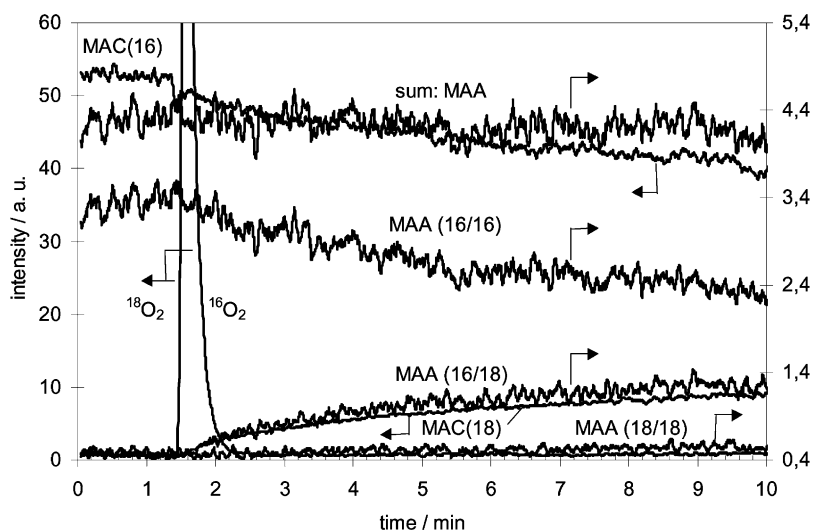

Fig. 11. Weight of sample 340 mg; volume-flow 20 ml min^{-1}; pre-treatment: 5 vol.% methacrolein and 15 vol.% $^{16}O_2$ in N_2, 300 °C, 180 min; experimental conditions: temperature 300 °C, 5 vol.% methacrolein and 15 vol.% $^{16}O_2$ or $^{18}O_2$ in N_2.

4. Conclusion

Under TP- and CP reduction conditions acrolein can activate more oxygen from the Mo/V mixed oxide than methacrolein. This may be due to the fact that methacrolein builds up a coke layer under a reductive atmosphere. The mechanism of the oxidation of the individual test-molecule to the corresponding acid-molecule, is identical. A distinction between the re-oxidation pathways of the oxygen surface vacancies (by gas phase oxygen to surface or by bulk diffusion to surface) is not yet possible.

CP reaction experiments (aldehyde $+ {}^{18}O_2$) show an unexpected exchange of the carbonyl oxygen of the aldehyde with the catalyst oxygen. After the exchange has occurred, the aldehyde can be desorbed from the surface of the solid, without reacting further. A subsequent re-adsorption and reaction can of course take place, too. A direct further reaction without prior desorption is also possible. Furthermore, this interesting exchange of carbonyl oxygen should be investigated more closely, in order to be able to present a better picture of the procedures on the surface of the catalyst.

Acknowledgements

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