

Dynamics of Bulk Oxygen in the Selective Oxidation of Acrolein

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Abstract: Gas phase oxidation of acrolein to acrylic acid on a hydrothermal prepared mixed oxide catalyst was investigated by steady state isotopic transient kinetic analysis (SSIKTA) as well as different types of concentration programmed techniques (CPR-Pulse, CPO) under in situ or process relevant conditions. Balancing the amounts of active oxygen gives an overview of the quantities of participating bulk oxygen species. The dynamics of bulk oxygen leads to re-oxidation processes on the catalyst surface and thus influences the selectivity pattern of the network of acrolein oxidation. Furthermore, the bulk-dynamics is activated by temperature.

Introduction

Acrylic acid (AA) is an important chemical intermediate.^[1] It is produced industrially by the partial oxidation of propene by a two-step heterogeneously catalysed process. The acrolein (ACR) formed in the first step is converted into AA on modified Mo/V/W mixed oxide catalysts in the second step. Currently, a selectivity of over 90 % can be achieved with industrial optimised catalyst systems. Carbon oxides, such as CO and CO_2 are formed as by-products from the combustion of ACR and AA.^[2]



Scheme 1. Reaction network of ACR oxidation.

In the past a lot of work has been done to identify and characterise the active catalytic phases.^[3] Often discussed are structure types like Mo_5O_{14} ,^[4] Mo_4O_{11} ,^[3a, 3b] Mo_6O_{21} among

others,^[3d, 3e] containing the metals molybdenum, vanadium and tungsten. However, it is known that the active site needs the interplay of molybdenum and vanadium, while the addition of tungsten leads to more stable catalysts.^[5] Tungsten also has an impact on the oxygen-mobility through the catalyst but does not take part in the redox-chemistry.^[3g, 6]

From a global perspective, the mechanism of the partial oxidation of ACR on mixed oxides follows the Mars-van Krevelen concept,^[7] which means that the reactant is oxidised by lattice oxygen and the reduced catalyst is re-oxidised by gas-phase oxygen.

For oxidations on mixed oxides it is generally shown, that the pathways of re-oxidation can be quite different. On the one hand, the reduced active-site can be re-oxidised directly by gasphase oxygen. On the other hand, it can be re-oxidised by bulk oxygen while the catalyst itself is re-oxidised at a separate active-site.^[8] In the latter case, the oxygen has to be transported from one site to another.^[9] A measurement of this oxygen transport under process relevant conditions is not trivial. It is well known that under steady state conditions, the selective catalyst surface is partially reduced and so the number of surface- and bulk-vacancies is different to the initial ones.^[10] Thus, it is important to measure the oxygen transport under process relevant conditions.

Generally, the oxygen transport can be measured by different methods, e.g. by secondary ion mass spectrometry (SIMS) on probes which are labelled with isotopic oxygen before,^[11] via x-ray imaging,^[12] or different temperature programmed methods.^[13] However, only few experiments performed in situ are mentioned in literature. One example is the oxygen diffusion in MgO at different degrees of surface reduction, where MgO was used as model catalyst for the oxidative methane dimerization.^[14] Another example is the work of Sokolovskii et al., who studied the oxygen transport of various mixed oxides at different degrees of reduction, with model reductants like CO or H₂.^[15]

In previous works we showed some oxygen pathways within the mechanism of ACR oxidation on Mo/V/W mixed oxides.^[2, 6b, 13b, 16] Predominantly results from transient response methods (TRM), especially in combination with isotopic assessment, enabled the observation of a fast oxygen exchange between ACR as reactant and oxygen from the catalyst lattice.^[2, 6b, 16b-e] This exchange reaction takes place via an equilibrium forming intermediately a surface acetal (ACR + 2 M-OH $\stackrel{\frown}{\longrightarrow}$ surface acetal + H₂O). From this key-intermediate the oxidation of ACR to an acrylate species or AA takes place subsequently, leaving an oxygen vacancy at the catalyst surface, which is reoxidised by gas phase or bulk oxygen.

Furthermore, results form SSTIKA and CPR led to the hypothesis that the degree of surface reduction significantly influences the selectivity pattern of the network of ACR oxidation. $^{[2, \ 13b, \ 16a, \ 16d]}$

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At this point it should be emphasised, that the previously mentioned results are all based on measurements on spray-

dried mixed oxides.^[6b, 13b, 16] Recently it was found, that the performance of hydrothermal prepared catalysts is significantly higher, which will be introduced within this contribution. The aim of this study is to investigate the participation of bulk oxygen in the ACR oxidation on such hydrothermal prepared catalysts in more detail. Both, SSITKA and CPR, especially as pulse-technique, are used in combination for balancing the amount of active oxygen under technical relevant or in situ conditions, respectively. Furthermore, temperature depended activation of the dynamics or participation of bulk oxygen as well as its influence on the catalytic performance is focussed.

Results and Discussion

As mentioned before, a lot of work has been done concerning the catalyst solid-science or structure.^[3] However, this study focuses on the dynamics of bulk oxygen and its participation in the catalytic cycle. In order to get more insight into the reaction-mechanism of the partial oxidation of acrolein, especially the dynamics of the bulk, a model catalyst is needed.^[17] Some requirements a model catalyst must meet are:

- simple composition (compared to the industrial catalyst)
- well-defined surface to bulk ratio
- thermal and redox stability
- high conversion and selectivity at industrial relevant conditions

One catalyst that fits all of the above criteria is the hydrothermal prepared $Mo_8V_2W_{0.5}O_x$ (21.5 < x < 30.5) mixed oxide. It was characterised to be non porous, nano-cristalline and has shown a high performance in the partial oxidation of acrolein as it is shown below.

Model catalyst and its steady state performance

The knowledge of the exact stoichiometry of the catalyst is needed for further investigation (oxygen balances, see below). Therefore, XPS (surface) and ICP (overall composition) analysis were made (Table 1).

Table 1. Composition of the catalytic material, measured with XPS and ICP. Normalised to the stoichiometric index of molybdenum of eight.				
Measurement	Мо	V	W	
XPS	8	1.8	1.1	
ICP-OES	8	1.5	0.6	

The stoichiometry of the resulting catalyst measured via XPS and ICP shows a slightly deviation from the target stoichiometry $Mo_8V_2W_{0.5}O_x$, which belongs to the stoichiometric composition of the initial precursor mixture (see experimental section).

Via the preparation route, nanoscale non-porous needle-like particles (Figure 1) are received. The particles exist of smaller rods. The rods have diameters between 40 and 100 nm and the needles are between 200 nm and 2 μ m in length. The specific surface area (BET, see experimental section) of the catalyst is 34 m² g⁻¹.



Figure 1. SEM-pictures of the hydrothermal prepared mixed-oxide catalyst with the formal stoichiometry $Mo_8V_2W_{0.5}O_x$.

Based on the observed particle shape, the catalyst fulfils the prerequisite of a well-defined surface to bulk ratio. This allows a more detailed investigation on the influence of the bulk for the selective oxidation of ACR.

XRD measurements after preparation, before and after certain treatments (pre-oxidised with O_2 and reduced with ACR), verified the redox stability of the catalyst (Figure 2).

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Figure 2. XRD of the hydrothermal prepared mixed oxide catalyst $(Mo_8V_2W_{0.5}O_x)$. As prepared, after pre-oxidation and after reduction with ACR.

The catalytic performance in terms of conversion (X) and selectivity (S) from steady state experiments is given in Figure 3.



Figure 3. Conversion and selectivity from steady state measurements for the oxidation of ACR to AA using a hydrothermal prepared Mo/V/W mixed oxide. Composition of the model catalyst was $Mo_8V_2W_{0.5}O_x$. Feed consists of 5 vol. % Acr and 10 vol. % O_2 (balance He). The catalyst mass was 50 mg and the total volume flow was 20 ml min⁻¹ (STP).

Under the chosen conditions (5 vol. % ACR and 10 vol. % O_2), the catalyst shows a performance of 83 % conversion and 89 % selectivity at 300 °C. Thus, the performance of the model catalyst is in the range of an industrial one.

All in all, this catalyst allows a more detailed investigation on the role of bulk oxygen in the partial oxidation of ACR.

¹⁸O₂-SSITKA

SSITKA (steady state isotopic transient kinetic analysis) give insights into the mechanism of catalytic reactions under real steady state conditions.^[16d, 16e] Here, ¹⁸O₂-SSITKA experiments were performed (exchange of ¹⁶O₂ against ¹⁸O₂ under global steady state) to get information about the participation of bulk oxygen in the selective oxidation of ACR.

In previous works $^{18}\text{O}_2\text{-}\text{SSITKA}$ experiments within ACR oxidation have already been presented with spray-dried

prepared mixed oxides ($Mo_8V_2W_{1.5}O_x$).^[16d] However, the spraydried oxide has two major disadvantages: On the one hand, its relative low BET-surface (4 m² g⁻¹), and on the other hand, the habitus of the particles. They are partially broken hollow spheres, and so do not have a well-defined surface to bulk ratio, which makes conclusions about the bulk participation quite difficult. Nevertheless, the main findings for the spray-dried oxide are summarised as follows:^[2, 6b, 16d]

- The sum of all components remains constant when ${}^{16}O_2$ is replaced by ${}^{18}O_2$, i.e. no kinetic isotope effect takes place.
- ACR exchanges its carbonyl oxygen with oxygen from the catalyst. Consequently, all isotopologues are formed.
- Oxygen exchange takes place via a surface-acetal (ACR).
- AA also exchanges its oxygen with the catalysts surface.

It should be emphasised that the ¹⁸O₂-SSITKA experiment in Figure 4 shows the result of the hydrothermal model catalyst and that the main findings are in accordance with those from the spray-dried catalyst.



Figure 4. Concentration profiles of an $^{18}O_2$ -SSITKA-experiment with 5 vol. % ACR and 10 vol. % O_2 at 300 °C. Total volume flow 20 ml min⁻¹ (STP). (50 mg Mo_8V_2W_{0.5}O_x). After 600 s $^{16}O_2$ is replaced by $^{18}O_2$. Soon after this replacement the formation of all isotopologues of the products can be observed. ^{18}ACR is formed due an exchange reaction with oxygen from the surface.

Additionally, the ¹⁸O₂-SSITKA reveals an opportunity to balance the quantities of elemental oxygen. Therefore, one has to calculate the elemental balances for ¹⁶O as well as for ¹⁸O. More precisely, here the elemental balance is defined as difference between the amount of substance entering the reactor and leaving it.

By balancing the amount of substance for 16 O during the ${}^{18}O_2$ phase, it can be observed that this balance is negative. This means more 16 O leaves the system than enters it. It follows that the missing amount of 16 O originates from the catalyst bulk,

which is the only remaining oxygen-source. One possible mechanistic explanation is illustrated in Scheme 2.



Scheme 2. Illustration of the bulk dynamics and the re-oxidation by gas phase oxygen during a SSITKA-experiment with ¹⁸O₂.

After adsorption and dissociation, the ¹⁸O can change its place with a ¹⁶O from the bulk in a hopping-like mechanism,^[18] resulting in a transport of ¹⁶O to the surface. So, more and more ¹⁶O can be removed from the catalyst by substitution with ¹⁸O. This is proofed by the ¹⁸O-balance, which is positive and in the same quantity like the missing ¹⁶O.

To get a concrete number of the bulk oxygen participation, the removed amount of ¹⁶O-oxygen ($n_{O,rem}$) is related to the amount of oxygen from the catalyst $(n_{O,cat})$. In this context, there are two interesting values to look at. The first is the potentially available oxygen $(n_{O,cat})$ and the second is the removable amount via redox processes (no, redox). Both can be calculated from the stoichiometry of the catalytic material and its mass. For the used model catalyst the high oxidised stoichiometry is $Mo_8V_2W_{0.5}O_{30.5}$ and the reduced one is $Mo_8V_2W_{0.5}O_{21.5},$ this is related to the oxidation states of the metals (Mo^{+VI}→Mo^{+IV} $V^{+\vee} \rightarrow V^{+\vee}$).^[3g] So, the available oxygen in the highest estimated oxidation state $(n_{0,cat})$ is about $1.05 \cdot 10^{-3}$ mole and for the lowest estimated oxidation state $0.742 \cdot 10^{-3}$ mole (related to 50 mg of the model catalyst). The difference between these two values is the amount of oxygen (0.3 · 10⁻³ mole) accessible via redox processes $(n_{O,redox})$. The latter is used for the CPR-Pulse experiments later, while the first is of interest for SSITKA.

The experimental identified amount (Figure 4) of removed ¹⁶O-oxygen ($n_{O,rem}$) was 0.12·10³ mole. This was removed from the catalyst within ten minutes at 300 °C. At a first glance, this does not seem very much but with respect to the overall amount of oxygen in the catalyst, this is about 11 % of the oxygen in the catalytic material ($n_{O,rem} \cdot n_{O,cat}^{-1}$) and 38 % of the oxygen which can take part in the redox processes ($n_{O,rem} \cdot n_{O,redox}^{-1}$). The results for SSITKA experiments at different temperatures are listed in Table 2.

Table 2. Amount of removed 16 O from 50 mg Mo ₈ V ₂ W _{0.5} O _{30.5} in the selective				
oxidation of ACR during an ¹⁸ O ₂ -SSITKA within ten minutes at different				
temperatures. $n_{O,cat}$ is the whole amount of oxygen in the catalyst. $n_{O,redox}$				
belongs to the oxidation states of the different metals				
$(Mo^{+VI} \rightarrow Mo^{+IV}; V^{+V} \rightarrow V^{+IV}; W \text{ does not take part in the redox processes}).^{[3g]}$				

	270 °C	300 °C	330 °C
n _{o,rem} / 10 ⁻⁶ mol	58.5	118	140
$n_{O,rem} \cdot n_{O,cat}$	0.06	0.11	0.13
$n_{O,rem} \cdot n_{O,redox}^{-1}$	0.19	0.38	0.45

With an increasing temperature the amount of ¹⁶O removed from the bulk within ten minutes increases. So, this is a kinetic effect where the bulk oxygen transport is activated by temperature. This shows the dynamics of the catalyst itself and the participation of bulk oxygen under steady state conditions. The results are in accordance with those from modelling of isotopologues pattern of previous SSITKA experiments.^[16d]

CPR-Pulse experiments

Reduction experiments also give the opportunity for balancing the removed oxygen from the catalyst. Especially the pulsetechnique with a variation of the pulse-distance provides insight in the dynamics of this process. So, Concentration Programmed Reduction-Pulse (CPR-Pulse) experiments with varying pulsedistances were performed at different temperatures with regard to selectivities of the individual reactions. These experiments show the importance of the degree of surface reduction for the selective oxidation of ACR and the oxygen mobility of the catalyst's oxygen.

The raw data of such an experiment are given as volume fraction for each component at a given time. The resulting volume fraction was transformed into a molar flow with the ideal gas law. Subsequent integration over time of each pulse results in the amount of substance of each component for each pulse. With these and the fed amount of ACR per pulse (verified by blank runs) the performance for each pulse is calculated. A typical response curve for a CPR-Pulse experiment as well as the integrated amount of substance for each component and the performance of the catalyst is shown in Figure 5.



Figure 5. Top: Response of a typical CPR-Pulse experiment. $1.15 \cdot 10^{-6}$ mole ACR per pulse, pulse-distance 60 s, temperature 300 °C and catalyst mass 100 mg Mo₈V₂W_{0.5}O_x. Middle: Integrated amount of substance per pulse for each component. Bottom: Calculated conversion (*X*), selectivity (*S*) and yield (Y) for the CPR-Pulse experiment.

The initial state of the catalyst is non-selective, caused by its high coverage with oxygen. The first five pulses only show combustion products. In the region of pulses ten to 18 the catalyst is very active and high selective. Needless to say that with an increasing amount of pulses the activity decreases due to the limited oxygen capacity of the catalyst. At pulse 50 the conversion decreases to values lower than 22 %. As a result of this experiment the selectivity towards AA depends on the degree of surface reduction (see also ^[2]).

In the next step we will follow the question whether the bulk oxygen participates, and if yes in which quantity, during the reduction experiments or not. In this context some prerequisites and assumptions will be given for calculating the relation between the amount of removed oxygen ($n_{O,rem}$) and oxygen on the surface of the catalyst ($n_{O,s}$). The surface oxygen can be estimated as follows.

The specific surface area of our model catalyst is 34 m²g⁻¹. Additionally, we assume that the catalyst exists of ideal crystals with the unit cell of a Mo₅O₁₄ phase. As described in literature, this is one of the active phases in the ACR oxidation.^[4] Furthermore, the smallest length of this unit cell is about 0.4 nm and can serve as the thickness of one surface-layer. With this and the BET surface, the volume of a surface-layer can be calculated.^[6b, 19] The ratio of this volume and the volume of the catalyst (see experimental section) should be the same as the ratio between the oxygen on the surface $(n_{0,s})$ and the whole oxygen of the catalyst $(n_{0,cat})$. It should be emphasised that this is only a concept which serves as a model. With these assumptions and the amount of oxygen in the catalytic material (described in the SSITKA section) one can calculate, analogically to the SSITKA experiments, the proportion of removed oxygen from the total surface-oxygen and the oxygen available via redox processes by this CPR-Pulse experiment (Table 3).

Table 3. Amount of oxygen removed from 100 mg $Mo_8V_2W_{0.5}O_x$ via CPR-Pulse experiment within 50 ACR pulses (each of $1.15 \cdot 10^{-6}$ mole ACR) at 300 °C and 60 s pulse-distance. $n_{O,s}$ stands for the overall oxygen from one surface-layer (assumed thickness 0.4 nm). $n_{O,redox,s}$ stands for the potentially available oxygen from one surface-layer via redox processes $(Mo^{+VI} \rightarrow Mo^{+IV}; V^{+V} \rightarrow V^{+IV}; W$ does not take part in the redox processes).^[3g]

n _{o,rem} / 10 ⁻⁶ mol	n _{o,s} / 10 ⁻⁶ mol	<i>n_{0,redox,s}</i> / 10 ⁻⁶ mol	n _{O,rem} •n _{O,s} ⁻¹	n _{O,rem} ∙ n _{O,redox.s}
64.6	118	34.9	0.54	1.85

The removed oxygen in the CPR-Pulse experiment with 50 ACR pulses (at 300 °C with a pulse-distance of 60 s) is more than the available oxygen from one surface-layer accessible via redox processes. This means that the overall amount of participating oxygen species of the catalyst is higher than the available amount of oxygen in the surface-layer. Thus, it is demonstrated that the bulk transports oxygen to the surface and provides this oxygen for the ACR oxidation.

Additionally, CPR-Pulse experiments with different pulsedistances were performed to look at the dynamics of bulk oxygen and the influence on the selectivity in more detail. Here, the distances between two pulses were varied between 60 and 240 s. The temperature for the reduction was kept at 300 °C.



Table 4. Amount of removed ^{16}O within 50 ACR pulses (each of $1.15\cdot 10^{-6}$ mole ACR) from the catalyst. Temperature 300 °C and 100 mg $Mo_8V_2W_{0.5}O_x$

Pulse-distance / s	n _{o,rem} / 10 ⁻⁶ mol	n _{0,rem} ∙ n _{0,s} ⁻¹	n _{O,rem} • n _{O,redox.s} -1
60	64.5	0.54	1.85
90	65.2	0.55	1.86
120	69.2	0.59	1.98
180	76.1	0.64	2.18
240	79.8	0.67	2.28

With an increasing time between two pulses the removed oxygen increases (Table 4). At higher pulse-distances the bulk is able to transport more oxygen to the surface and to provide this for the oxidation of ACR. Additionally, it can be observed that the selectivity towards AA decreases with an increasing time between two pulses. This demonstrates the effect of surfaceoxygen on the selectivity. Due to a higher coverage of oxygen the selectivity decreases with an increasing pulse-distance. The higher the pulse-distance, the lower is the selectivity towards AA Consistent with this, the conversion of acrolein increases with an increasing pulse-distance. The earliest detection of AA is at pulse number five. This is due to the fact that the catalyst in its initial state is covered with "non-selective" oxygen and the formed acid is oxidised directly towards the combustion products This was cross-checked in additional experiments with AA pulses

As shown in Figure 6, the theory fits the experimental measured data. In other words, with a variation of the pulsedistance two theses are verified: On the one hand, the reoxidation of the surface by bulk oxygen and, on the other hand, the connection between the degree of surface reduction and the selectivity of the catalyst.

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Figure 6. Conversion and selectivity for each pulse at different pulse-distances. Temperature 300 °C and 100 mg $Mo_8V_2W_{0.5}O_x$. Initial amount of ACR per pulse $1.15\cdot 10^{-6}$ mole.

By looking at the response curves for the remaining products (AcOH, CO, CO₂, H_2O), one additional phenomenon can be observed: The formation of carbon monoxide shows an interesting trend which is independent from the pulse-distance. The formation of carbon monoxide can be detected until the first ten pulses. With higher pulse numbers no considerable amount of CO can be detected (Figure 7).



Figure 7. Selectivity of carbon monoxide for each pulse at different pulse-distances at 300 °C and 100 mg $Mo_8V_2W_{0.5}O_x$. Initial amount of ACR per pulse $1.15\cdot 10^{-6}$ mole.

These results give hint for at least two active sites – one for the selective oxidation and another for the combustion towards CO. However, the second active site is either not in contact with the bulk or its re-oxidation by bulk oxygen is too slow at the investigated temperatures.

Additionally, the elemental balances were checked, defined as the ratio between the overall detected amount of an element leaving the reactor and entering it. The carbon balance (Figure 8) is overall lower than one, which means that more carbon is entering the reactor than leaving it. So, there must be some kind of formation of coke or undetected products. However the elemental balance shows a minimum in the range of pulse six and nine. After that, it increases with an increasing number of pulses and reaches a level in the range of 90 %, decreasing with higher pulse-distance.



Figure 8. Carbon balance for each pulse at different pulse-distances at 300 °C and 100 mg $Mo_8V_2W_{0.5}O_x$. Initial amount of ACR per pulse1.15·10⁻⁶ mole.

As mentioned above, the carbon balance increases with a decreasing pulse-distance. According to the theory of a more non-selective oxidation with higher pulse-distances, the carbon balance is lower and so the formation of coke or undetected products is higher (more non-selective oxidation). However, there is some carbon missing. To clarify the disposition of missing carbon, the catalysts were re-oxidised for one hour at 400 °C with 10 vol. % oxygen (CPO) after the reduction pulses (Figure 9).

The amount of removable carbon from the catalyst during a CPO is nearly the same for all pulse-distances. Nevertheless, with a higher pulse-distance the formation of undetected products or irreversible coke-deposits increases. By calculating the ratio between the overall missing carbon (difference between missing carbon after pulses and the detected carbon after CPO) and the fed carbon, the carbon-recovery is accessible. The experiment with a pulse-distance of 60 s has a carbon-recovery of more than 99 %, while the experiment with a distance of 240 s has a carbon-recovery of 92 %. So, the formation of a reversible coke-layer is independent from the pulse-distance, while the formation of undetected products and/or irreversible coke depends on the distance. However, this also confirms the result of a more non-selective oxidation at a higher oxidised surface.



Figure 9. Integrated amount of carbon in dependence of pulse-distance. Square: Missing carbon after 50 ACR reduction pulses. Triangle: Detected carbon during re-oxidation (CPO). 100 mg $Mo_8V_2W_{0.5}O_x$. Initial amount of ACR per pulse1.15 \cdot 10⁻⁶ mole.

With these experiments the participation of bulk oxygen in the selective oxidation is evidenced. It is shown that the transport of oxygen from the bulk to the surface of the catalyst is measurable.

Additionally, the CPR-Pulse experiments were performed at different temperatures (Figure 10).



Figure 10. Removed oxygen from the catalysts by 50 ACR-pulses at different temperatures and pulse-distances. 100 mg $Mo_8V_2W_{0.5}O_x$. Initial amount of ACR per pulse1.15·10⁻⁶ mole.

With an increasing temperature, the removable oxygen from the catalyst increases. This result is in accordance with the one from the ¹⁸O₂-SSITKA experiments where the bulk oxygen transport is also activated with temperature. Additionally, it can

be seen that for each temperature an increase of the pulsedistance leads to more removable oxygen.

Due to the different types of experiments, steady state reaction (SSITKA) where the oxygen is replaced and not really removed like it is in the reduction experiments (CPR-Pulse), the overall amount of removed oxygen from the catalyst is quite different. Nevertheless, the SSITKA-values can serve as a reference for the CPR-Pulse experiments and also proof the result of a kinetic effect in the bulk oxygen transport.

Conclusions

The dynamics of bulk oxygen in the selective oxidation of acrolein were investigated on a Mo/V/W mixed oxide by using two different transient response methods under in situ conditions For the first time a comparable study of the bulk-dynamics under steady state and under reductive conditions has been performed

In summary, the results of SSITKA-experiments and CPR-Pulse experiments evidence that bulk oxygen plays an important role in the partial oxidation of ACR. It is shown that the transport of oxygen from the bulk to the surface of the catalyst can be measured with these kinds of experiments. Thus, a calculation of the participating active oxygen is feasible.

In addition to this, it is shown that a more reduced surface leads to a more selective but less active oxidation. So, there exists an optimal degree of surface reduction, low for high selectivity but high enough for sufficient activity. However, the degree of surface reduction is influenced by bulk oxygen, so the bulk oxygen transport is essential for the catalytic performance.

Moreover, the formation of undetected products and/or irreversible coke-layer also depends on the degree of surface reduction or the bulk oxygen transport, respectively.

Furthermore, these experiments give hint for at least two active sites: A selective one, which is in contact with the bulk and one for the combustion to carbon monoxide, which is (at the investigated temperatures) not re-oxidised by bulk oxygen.

Thus, the CPR-Pulse experiments can give access to the kinetics of the bulk-processes under reaction near conditions. For this reason, CPR-Pulse experiments are a powerful tool to characterise different oxygen contents and mobility under more reaction relevant conditions.

Experimental Section

Catalyst preparation and characterisation:

The catalyst with the general formula $M_{08}V_2W_{0.5}O_x$ (21.5<x<30.5) was prepared via hydrothermal synthesis according to the patent specification DER10 2012 207 811 A1.^[20] An aqueous solution containing ammonium heptamolybdate (11.3 g) and ammonium metatungstate (1.1 g) were dissolved in distilled water (120 ml). Vanadyl sulfate hydrate(4.2 g) was also dissolved in distilled water (120 ml). These two solutions were mixed and adjusted to a pH value of 2.0 with sulfuric acid (9 M) and transferred in an autoclave (teflon inner tube). After bubbling with N₂ for ten minutes the stirred reaction mixture was heated up to 448 K with 5 K min⁻¹ and maintained at this temperature for 24 h under hydrothermal conditions.



After cooling the crude product was filtered, washed with water and taken up in 120 mL of a 0.4 mol l^{-1} oxalic acid solution. The obtained suspension was stirred for 1 h at 353 K. Subsequent the solid was filtered, washed with distilled water again and dried overnight at 353 K.

The BET specific surface area of the catalyst was measured from the N₂ sorption isotherms collected on a Quantachrome Quadrasorb at 77 K. Prior to the measurement, the sample was degassed at 300 °C until a stable vacuum of approximately $1.3 \cdot 10^{-5}$ bar was reached. The catalyst was characterised to be non-porous with a specific surface area of $34 \text{ m}^2 \text{ g}^{-1}$ (Figure 11).



Figure 11. Results of the N2-physisorption measurement of M08V2W0.5Ox.

SEM data were obtained with an FEI XL30 FEG microscope from Philipps with an acceleration voltage of 10 kV.

XRD patterns were collected with an Empyrean diffractometer from PANalytical equipped with a CuK α radiation (λ =0.15 nm), at a step width of 0.013° in the (2 θ) range from 5° to 70°.

XPS data were obtained with an SSX 100 ESCA electron spectrometer from Surface Science Laboratories Inc. using 90 W $AI_{K\alpha}$ radiation. The base pressure was about $3\cdot 10^{-9}$ mbar.

ICP-OES data were obtained with an ICP Optima 300 spectrometer from Perkin Elmer. Prior to the measurement 20 mg catalyst were solved in 20 mL 1 M NaOH. The resulting solution was then diluted with H_2O in a ratio of 1:100.

Table 5. Data of surface-layer.	the catalytic	material needed	I for the calc	culation of a
He-density ^[a] / g cm ³	BET / m ² g ⁻¹	V _{catalyst} ^{(b]} / 10 ⁻⁹ m ³	V _{surface} ^[c] / 10 ⁻⁹ m ³	V _{surf.} ·V _{cat.} -1 ∕ %
4.131	34	0.24	1.36	5.62

[a] measured by Quantachrome with a Poremaster 60-GT according to DIN 66133. [b] of 100 mg $Mo_8V_2W_{0.5}O_x$. [c] with the approximation of a surface-layer thickness of 0.4 nm.

Kinetic investigations:

Reactor apparatus:

All experiments were carried out on a self-constructed apparatus for kinetic investigations, which allows fully automatic changes in temperature- and concentration-programmed reactions (flow sheet see Supporting Information). It consists of three main parts: a gas dosing unit, a reactor and an online analytic. The gas dosing was realised with an arrangement of several mass flow controllers, multiway-valves and twostage gas saturators, allowing a flexible dosage of gaseous and liquid components. Additionally, a 6-way-valve with a 1 mL sample loop allows pulse-wise dosing of components. A quartz U-tube (internal diameter 4 mm) served as the reactor, in which the catalyst was fixed between two quartz wool stoppers. The reactor was placed in an electrically heated oven, which was temperature controlled. The reaction gas was analysed online via mass spectrometry (GAM 400, InProcess Instruments, Germany). All experiments were performed under continuous flow (overall volume flow 20 mL min⁻¹ (STP)) at ambient pressure. The common catalyst masses were 50 or 100 mg. Helium was used as inert carrier gas.

Catalyst pre-treatment:

Before the measurements, the catalyst was pre-treated for 1 h at 400 $^\circ$ C with oxygen (10 vol. % in He). The purpose of this oxidative pre-treatment was to achieve a specific oxidation and reproducible initial state.

Steady State Performance:

After the pre-treatment, the catalyst was cooled down to 100 °C in a constant helium flow of 20 mL min⁻¹ (STP). After reaching this temperature the gas was switched to feed composition (5 vol. % ACR and 10 vol. % oxygen) and was kept until steady state concentrations were detected (several hours). Then subsequently the temperature was raised to the next level. The experiment was performed at 100, 150, 200, 225, 250, 270, 300, 330, and 360 °C.

SSITKA experiments:

Following the pre-treatment, the catalyst was cooled down to 270 °C in a constant helium flow of 20 mL min⁻¹ (STP). Then, the reaction gas (5 vol. % ACR and 10 vol. % oxygen) was lead over the catalyst until steady concentrations were detected (several hours). Data acquisition was initialised and ¹⁶O₂ was replaced by ¹⁸O₂ after 10 min and vice versa after 20 min. The measurement was terminated after in total 30 min. The temperature was increased to the next level with a heating rate of 2 K min⁻¹. After steady state was reached the next SSITKA experiment (¹⁶O₂ \rightarrow ¹⁸O₂ \rightarrow ¹⁶O₂) was performed. The exchange was carried out at 270, 300, 330 °C.

CPR-Pulse experiments:

Following the pre-treatment, the catalyst was cooled down to the desired temperature under a constant helium flow of 20 mL min⁻¹ (STP). The overall volume flow is separated into two with 10 mL min⁻¹ (STP) each. One of these is used for flushing the sample loop of the 6-way-valve (Figure 12). The feed gas for the sample loop exists of 5 vol. % ACR (or 2.5 vol. % AA) in He with a total volume flow of 20 mL min⁻¹ (STP). With an automated plant control (LabView®) it is possible to switch the 6-way-valve with defined time steps (60, 90, 120, 180, 240 s). The CPR-Pulse-experiments were carried out at 270, 300, 330 °C.



Figure 12. Scheme of the 6-way-valve with gas flow and two states. Position A is for loading the sample loop and position B for flushing.

Blank runs were made to verify the initial amount of aldehyde per pulse. They were performed for every pulse-distance and for each temperature.

CPO experiments:

Following a CPR-Pulse experiment the catalyst was heated up to 400 °C with a rate of 10 K min⁻¹ under 20 mL min⁻¹ (STP) He flow. After reaching this temperature the catalyst was re-oxidised for one hour by switching to an oxidising atmosphere (10 vol. % O_2 in He).

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Keywords: acrolein • heterogeneous catalysis • mixed oxides • oxidation • bulk oxygen • SSIKTA • pulse-technique

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Entry for the Table of Contents

FULL PAPER

Gas phase oxidation of acrolein to acrylic acid on a hydrothermal prepared mixed oxide catalyst was investigated by SSIKTA and concentration programmed techniques (CPR-Pulse, CPO) with respect to technical relevant conditions. Balancing the amounts of active oxygen gives an overview of the quantities of participating bulk oxygen species. The dynamics of bulk oxygen leads to re-oxidation processes on the catalyst surface and thus influences the selectivity pattern of the network of acrolein oxidation.



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Dynamics of Bulk Oxygen in the Selective Oxidation of Acrolein

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