Mode of action of oxidation-active centres in Mo–V mixed oxides on the partial oxidation of an unsaturated aldehyde

Herbert Vogel [a,*], Ralf Böhling [b] and Hartmut Hibst [b]

[a] *Institute of Chemical Technology, Department of Chemistry, Darmstadt University of Technology, Petersenstrasse 20, D-64287 Darmstadt, Germany*
[b] *BASF AG, D-67056 Ludwigshafen, Germany*

Received 20 March 1999; accepted 20 July 1999

The mode of action of the oxidation-active centres in Mo–V mixed oxides on the selective oxidation of an unsaturated aldehyde was investigated by non-steady-state methods. Various oxidation-active centres, differing in activity and selectivity, were identified by non-steady-state methods. In addition, the influence of the crystallinity of the Mo–V mixed oxides on the activity and selectivity properties were investigated. It was shown that, in contrast to crystalline samples, only X-ray-amorphous Mo–V mixed oxides contained selective oxidation centres. The measurements were used to derive a model based on the interaction of active centres with various redox properties.

Keywords: selective oxidation, molybdates, vanadates, acrolein, acrylic acid, temperature-programmed methods, concentration-programmed methods

1. Introduction

The heterogeneously catalyzed partial oxidation of unsaturated hydrocarbons is an important reaction class for the synthesis of many key products and intermediates in the chemical industry. Besides metallic systems, the main catalysts used are solid-state oxide systems. As a rule, these can store oxygen reversibly. Selective oxidation of the organic educt takes place as a result of the oxygen stored in the catalyst, various oxygen species being capable of oxidative activity. The catalyst is re-oxidized by molecular gas-phase oxygen (Mars–van Krevelen mechanism [1]). The catalysts investigated were molybdenum–vanadium mixed oxides, which are the basic material for many industrial catalyst systems. Acrolein served as an example of an unsaturated aldehyde.

Schlögl et al. [2] used thermal analysis and transmission electron spectroscopy (TEM) to investigate the conversion of molecular gas-phase oxygen to active lattice oxygen on Mo–V mixed oxides. The purpose of the present work was to employ non-steady-state methods to obtain a deeper insight into the mode of action of the different types of oxidation centres (selectivity/activity behaviour as a function of temperature) in such catalyst systems. On the one hand, non-steady-state methods such as temperature-programmed reaction, reduction and oxidation (TP measurements) were used. In addition, isothermic concentration-programmed methods (CP measurements) were used, in which the interference factor was not the usual temperature, but the educt/product concentration (jump or pulse). A review of these non-steady-state methods is given in [3]. By means of these non-steady-state investigation methods, the individual reduction/oxidation reactions on the catalyst system could be separated and characterized with regard to their activity and selectivity properties. Such information is difficult to obtain by steady-state kinetic experiments or traditional surface test methods.

2. Experimental

2.1. Catalysts

Tests were carried out with three Mo–V mixed oxides:

Sample 1: crystalline Mo–V mixed oxide with the composition $Mo_{0.8}V_{0.2}O_x$ and crystal structure of hexagonal MoO_3 [7]; BET surface area 5.7 $m^2\,g^{-1}$; XRD spectrum figure 1(a).

Sample 2: X-ray-amorphous Mo–V mixed oxide with the composition $Mo_{0.8}V_{0.2}O_x$; BET surface area 6.6 $m^2\,g^{-1}$; XRD spectrum figure 1(b). Additional investigations by high-resolution electron transmission microscopy (HR-TEM) confirm a disordered structure [2].

Sample 3: X-ray-amorphous Mo–V mixed oxide; BET surface area 19 $m^2\,g^{-1}$.

The samples were synthesized by thermal decomposition of the corresponding ammonium salts under oxygen of a specific partial pressure [2,4]. Thermal treatment at temperatures <400 °C resulted in X-ray amorphous structures (sample 2). At higher temperatures (>450 °C) and oxidizing gas atmospheres crystalline samples with the structure of hexagonal MoO_3 were formed (sample 1).

---

[*] To whom correspondence should be addressed.

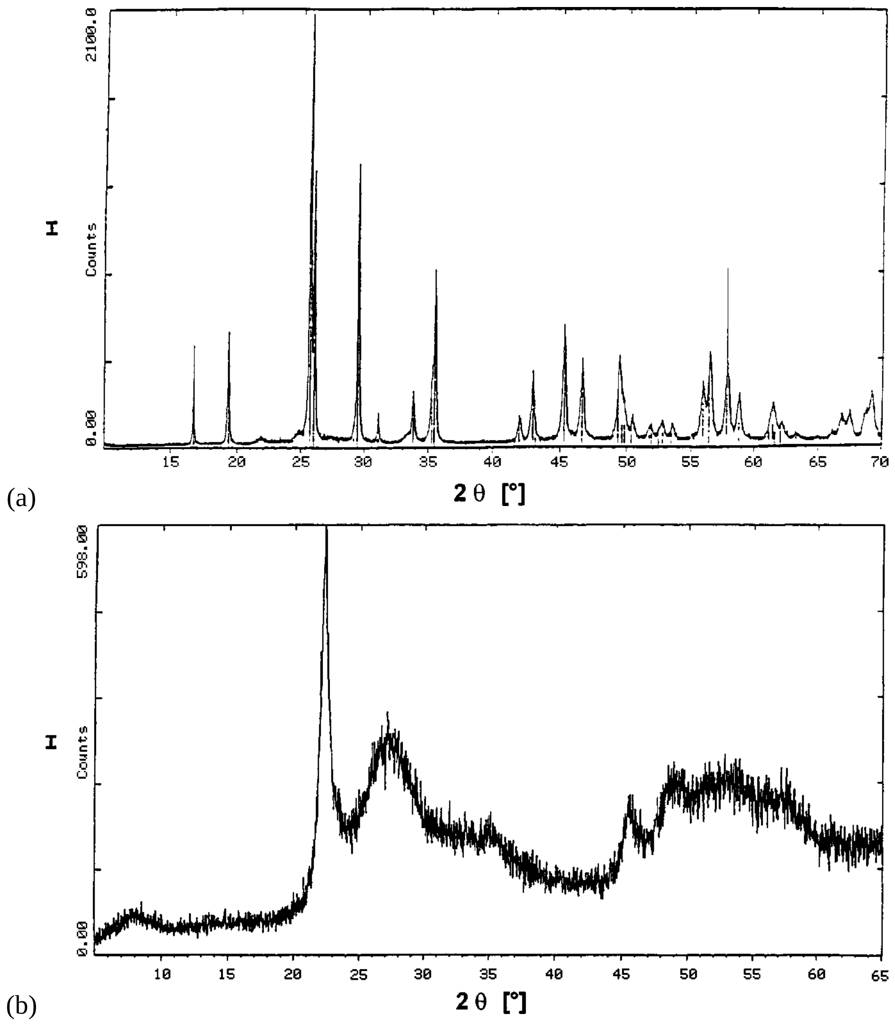

Figure 1. (a) X-ray diffractogram of sample 1 (crystalline $Mo_{0.8}V_{0.2}O_x$, BET surface: 5.7 m^2); (b) X-ray diffractogram of sample 2 (amorphous $Mo_{0.8}V_{0.2}O_x$, BET surface: 6.6 m^2).

2.2. Non-steady-state experiments

Construction of the apparatus for carrying out the non-steady-state experiments is explained in detail in [3,5]. The experimental procedure for the TP and CP measurements was divided into *in situ* pretreatment of the samples and the actual measurement. The sample was pretreated at a specific temperature and gas-phase composition to bring it into a specific, reproducible initial state with regard to its degree of oxidation and surface substances. The gas composition was analyzed on-line by QMS.

2.3. Pretreatment of the samples

Before the TP measurements were made, the samples were pretreated for 1 h at 270 °C with oxygen (10 vol% O_2 in N_2). The purpose of this oxidative pretreatment was to achieve a specific oxidation state and to remove surface impurities.

2.4. TP reduction

After pretreatment of the samples, the TP reduction reactions were carried out with 5 vol% acrolein in N_2 at a heating rate of 10 $K\,min^{-1}$ in the temperature range of 90–500 °C.

2.5. TP oxidation

After pretreatment, the samples were treated for 1 h at 290 °C with acrolein (5 vol% in N_2) or 9 h with a reaction gas mixture (5 vol% acrolein, 10 vol% O_2 and 5 vol% H_2O, the remainder N_2). The samples were then oxidized with oxygen (10 vol% in N_2) at a heating rate of 10 $K\,min^{-1}$ in the temperature range of 90–550 °C. The oxygen consumption was determined by WLD.

2.6. TP reactions

The TP reactions were carried out analogously to the TP reduction reactions. However, the reactive gas consisted of a mixture of 5 vol% acrolein, 10 vol% oxygen and 5 vol% water in nitrogen, and the heating rate was 5 $K\,min^{-1}$.

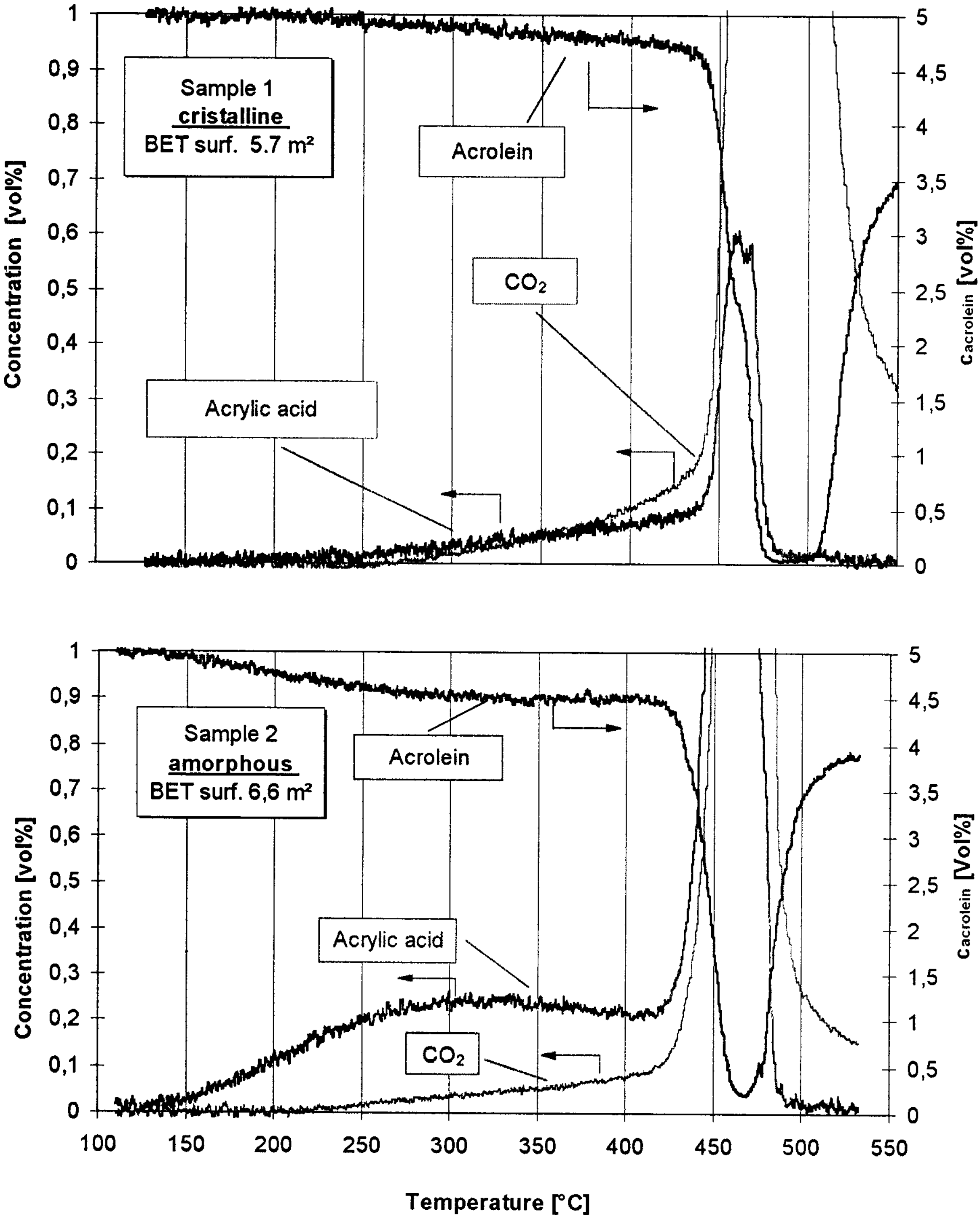

Figure 2. TP reduction spectra of the products formed (in vol%) as a function of temperature when X-ray-amorphous sample 2 and crystalline sample 1 were heated. Pretreatment: 60 min with 10 vol% O_2 in N_2 at 270 °C; sample weight: 91 mg; reaction gas: 5 vol% acrolein in N_2; flow rate: 20 ml/min; heating rate: 10 °C/min.

2.7. CP reactions

In the concentration-programmed experiments the concentration pulses were produced by six-way pneumatic valves. After the usual sample pretreatment followed by purging for 60 min with nitrogen, an educt/product concentration pulse was applied at isothermic conditions.

3. Results and discussion

Samples 1 and 2, with comparable chemical composition and BET surface area (approximately 6 $m^2\,g^{-1}$), showed, in accordance with their different crystallinities, large differences with respect to the selective partial oxidation of acrolein. The TP reduction spectra in figure 2 show that the amorphous sample provided considerably more selec-

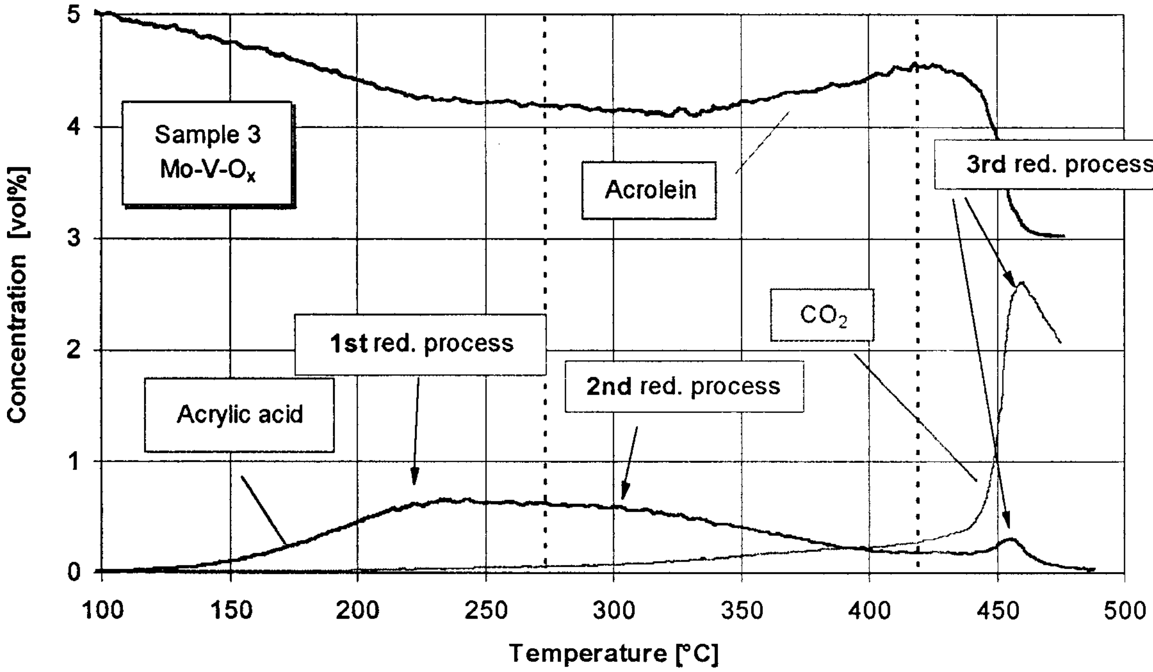

Figure 3. TP reduction with acrolein of sample 3 (Mo–V–O) (red. = reduction). Pretreatment: 60 min with 10 vol% O_2 in N_2 at 350 °C; sample weight: 90 mg (sample 3), reaction gas: 5 vol% acrolein in N_2; flow rate: 20 ml/min; heating rate: 10 °C/min.

tively acting oxygen for the partial oxidation of acrolein to acrylic acid than the crystalline sample did. Both samples behaved similarly at temperatures above approximately 400 °C with regard to total oxidation to CO_2.

This behaviour was confirmed by steady-state measurements in an integral reactor under industrial plant conditions (5 vol% acrolein, 10 vol% O_2, 5 vol% H_2O, the remainder N_2). The crystalline sample formed acrylic acid at a much lower rate than the amorphous sample, with a similar rate of formation of the complete-oxidation products. The comparison showed that only X-ray-amorphous Mo–V mixed oxides exhibit a significant catalytic activity for the formation of acrylic acid. As a result, we describe the findings of more detailed investigations of the various oxidation-active centres of sample 3 (X-ray-amorphous Mo–V–O), which has three times the specific surface of samples 1 and 2. This BET surface is comparable with values of industrially used catalysts.

3.1. TP reduction with acrolein

The TP reduction spectra (figure 3) of X-ray-amorphous sample 3 shows three maxima for the formation of acrylic acid (corresponding to three reduction processes). Comparing the conditions corresponding to these maxima (CO_2 and acrylic acid) indicated that only the low-temperature peaks (240 and 300 °C) resulted in selective acrylic acid formation. The amount of acrylic acid formed indicates that the bulk oxygen is involved in oxidation of the aldehyde. This is in accordance to the postulated Mars–van Krevelen mechanism.

3.2. TP oxidation reactions

In contrast to the reduction reactions mentioned above, TP oxidation was used to test the oxygen absorption of a sample reduced with acrolein at 290 °C. Figure 4 shows the TP oxidation spectrum of sample 3 (X-ray-amorphous Mo–V–O). The three peaks can be assigned to three processes all incorporating oxygen. Reduction and re-oxidation of the catalyst is reversible up to 390 °C. This is shown by cyclic CP experiments, described in the following section. However, in interpreting this figure it should be remembered that the oxygen consumption depends not only on the oxygen incorporation of the solid but also on oxidation of surface adsorbates to CO_x.

The first two peaks are at 290 (first oxidation process) and 360 °C (second oxidation process). The peak at 480 °C (third oxidation process) can be attributed to the oxidation of V^{4+}. A fresh catalyst shows this peak too, even when it is pretreated with oxygen. According to Andrushkevich [6], at temperatures over 450 °C the mixed oxide is destroyed, forming V_2MoO_8 and MoO_3.

3.3. CP measurements

The first and second oxidation processes were characterized in greater detail by means of cyclic CP measurements with acrolein. This involved feeding acrolein repeatedly stepwise (5 vol% in N_2) onto the same sample at 290 °C. In between the acrolein jumps, the sample was purged with nitrogen and re-oxidized alternately at 290 and 390 °C with oxygen (10 vol% in N_2). A diagram of the experimental procedure is given in figure 5.

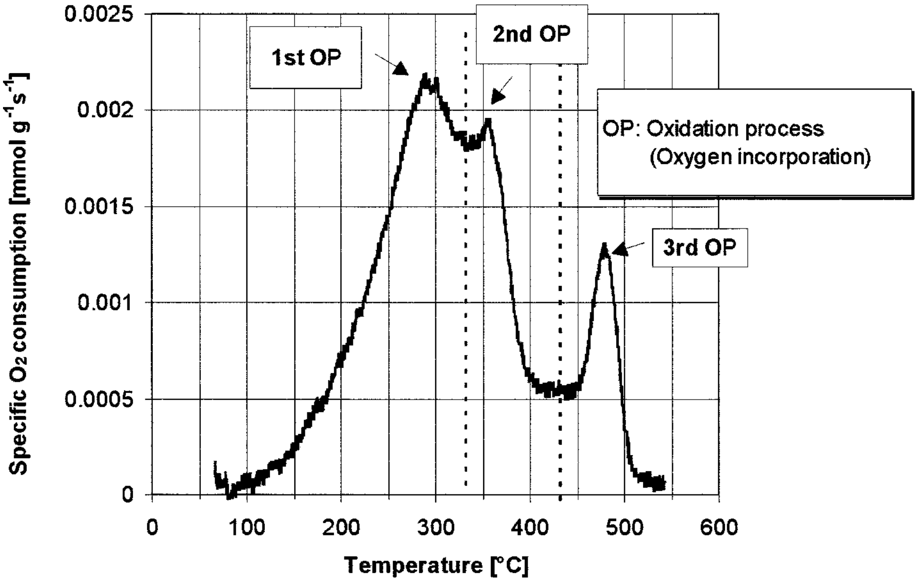

Figure 4. TP oxidation spectra of sample 3 (Mo–V–O). Pretreatment: 60 min with 5 vol% acrolein in N_2 at 290 °C; sample weight: 100 mg; reaction gas: 5 vol% O_2 in He; flow rate: 36 ml/min; heating rate: 10 °C/min.

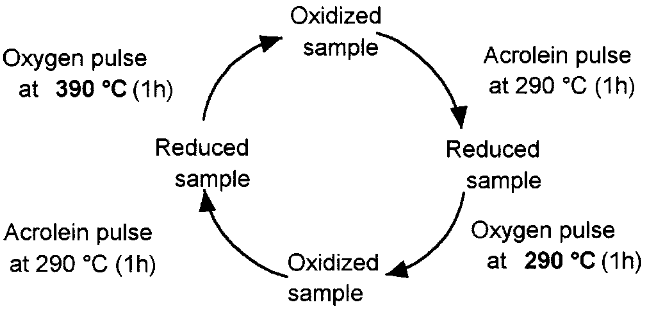

Figure 5. Experimental sequence of cyclic step responses.

The re-oxidation temperature of 390 °C exceeds that of the two re-oxidation processes, whereas the re-oxidation temperature of 290 °C lies below that of the second re-oxidation process and within the range of the first (see figure 4). The diagram of figure 6 shows an acrolein jump after re-oxidation at 390 °C, and the lower diagram an acrolein jump after re-oxidation at 290 °C. The acrolein jump responses obtained during one cycle, an example of which is represented in figure 6, change only very slightly during many cycles with the same sample, while the total amount of oxidation-active oxygen decreases with increasing cycle number.

From figure 6 it can be seen that only after re-oxidation at 290 °C acrylic acid is selectively formed from acrolein. This must be caused by the oxygen species of the so-called first oxidation process, since the oxygen centres of the second oxidation process were not yet re-oxidized at a temperature of 290 °C (figure 4). Treatment with oxygen at 390 °C also re-oxidized the “higher” centres (second oxidation process). First, one can see a sharp CO_2 peak and then the acrylic acid formation follows. Therefore, the total-oxidation products were caused by the oxygen species of the first reduction process (see figure 3), which is coupled with the second oxidation process (see figure 4). The second reduction process is coupled with the first oxidation process, which further oxidizes acrylic acid in a secondary reaction.

3.4. TP reactions

To further elucidate the interaction of the reduction and oxidation processes, TP reaction measurements were carried out while the reaction mixture (acrolein/O_2/H_2O) flowed over the sample and a temperature ramp was applied. These measurements provide a qualitative impression of the activity/selectivity properties as a function of temperature. Figure 7 shows the corresponding TP reaction spectrum of X-ray-amorphous sample 3 (Mo–V–O).

The TP reaction spectrum can be roughly divided into three temperature ranges (I, II, III). It is noteworthy that no acrylic acid is formed in range I (100–200 °C). This is initially surprising, because acrylic acid formation in the TP reduction reactions (see figure 3) already begins above 150 °C, and, according to figure 4, re-oxidation begins above 100 °C.[1] This means that in the case of the first reduction process replenishment with molecular gas-phase oxygen closes the catalytic cycle only when the temperature exceeds 200 °C. This is the temperature range of the second oxidation process. The first reduction process can therefore be assigned to the second oxidation process and vice versa.

In range II (200–330 °C), acrylic acid is formed with high selectivity. In this temperature range, the second reduction process selectively oxidized acrolein to acrylic acid,

---

[1] Because of the lower heating rate and lower sample weight of the TP reactions compared with the TP reduction reactions, only 1/10 of the signal intensity of the oxidation products of the TP reactions was due to the stored lattice oxygen, so that the oxygen capacity of the catalyst contributed only imperceptibly to product formation.

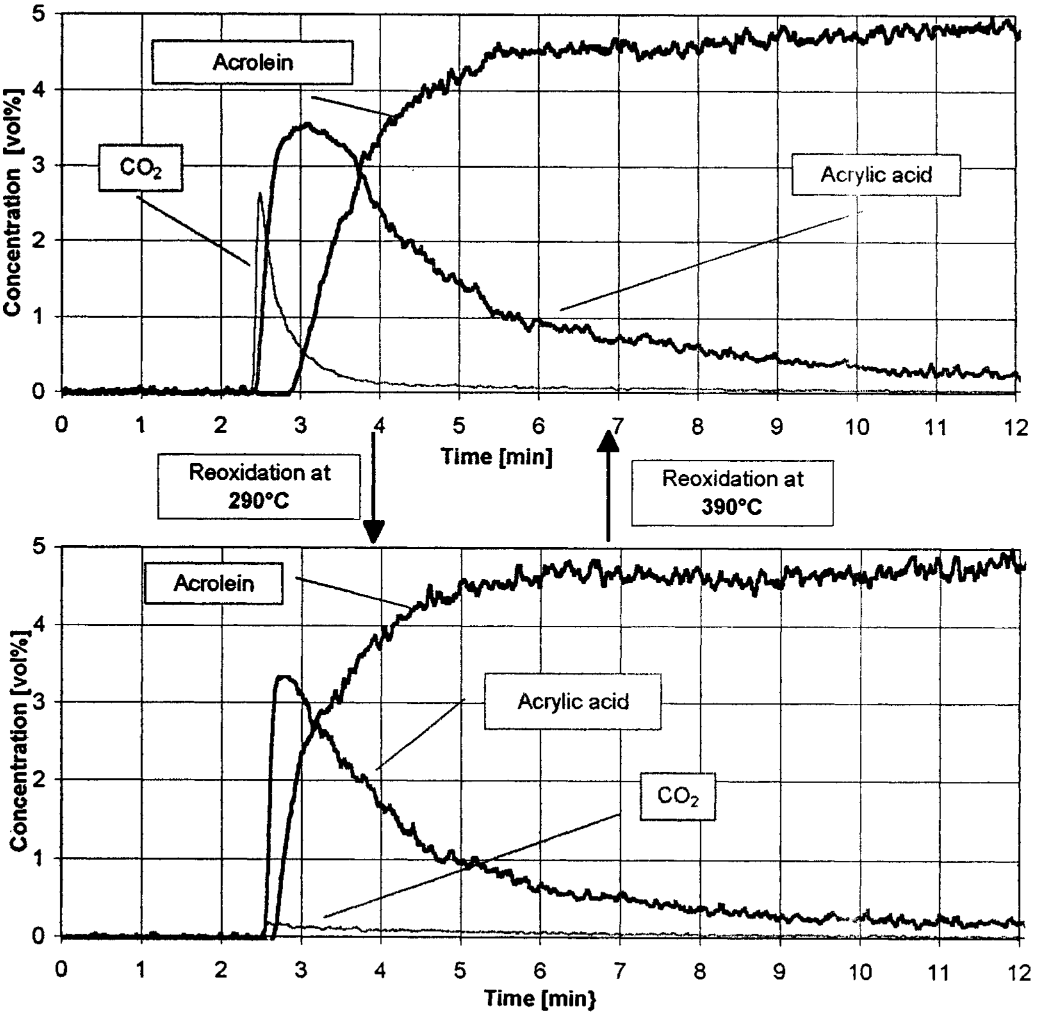

Figure 6. Cyclic jump responses measured in sample 3 following isothermic acrolein concentration jump at 290 °C. The upper graph shows jumps after isothermic treatment with oxygen at 390 °C, and the lower graph after treatment at 290 °C. Pretreatment: 60 min with 10 vol% O_2 in N_2 at 350 °C; sample weight: 100 mg; reaction gas: 5 vol% acrolein in N_2; flow rate: 20 ml/min.

as shown in figure 3. The supply of active lattice oxygen is permanently maintained by the first oxidation process (see figure 4), which can incorporate molecular gas-phase oxygen into reduced lattice structures once the temperature exceeds 150 °C. Because the first oxidation process starts approximately 50 °C below the second reduction process, the re-oxidation rate (obtained by TP measurements) at 290 °C (industrial conditions) is about six times as great as the reduction rate (by TP measurements) of the catalyst with acrolein. It can therefore be assumed that a high oxidation state will be achieved under industrial plant conditions ($T \approx 290$ °C). A high oxidation state prevents the selectivity from being adversely affected by coking of the catalyst, for coke products, once formed, block the surface and are only eliminated by total oxidation (to an appreciable degree only above 300 °C).

At higher temperatures (range III), the oxygen species of the second oxidation process (see figure 4) are incorporated, allowing the first reduction process to proceed again. As described above, the coupling of these two processes leads to secondary oxidation of the acrylic acid.

If the O_2 curve is considered in terms of the above ranges, a steady increase in O_2 consumption rate is observed as expected at temperatures above 200 °C. Naturally, with falling acrolein concentration (above 290 °C) a turning point in the O_2 consumption rate is reached. Above 330 °C the curve again changes its slope and becomes increasingly steeper despite decreasing acrolein concentration. The reason is that above this temperature the first reduction process is again supplied with lattice oxygen by the now-proceeding second oxidation process, so that the acrylic acid, present in high concentration, can be completely oxidized by the first reduction process.

To obtain further information, runs were carried out under industrial, steady-state conditions [4] and subsequently TP oxidation spectra were recorded. Figure 8 shows a comparison of TP oxidation after pretreatment with 5 vol% acrolein in N_2 and after pretreatment with a gas mixture corresponding to industrial plant conditions. Measurements after the latter pretreatment showed oxygen incorporation only for the second oxidation process. This confirms that although these oxygen species are consumed under indus-

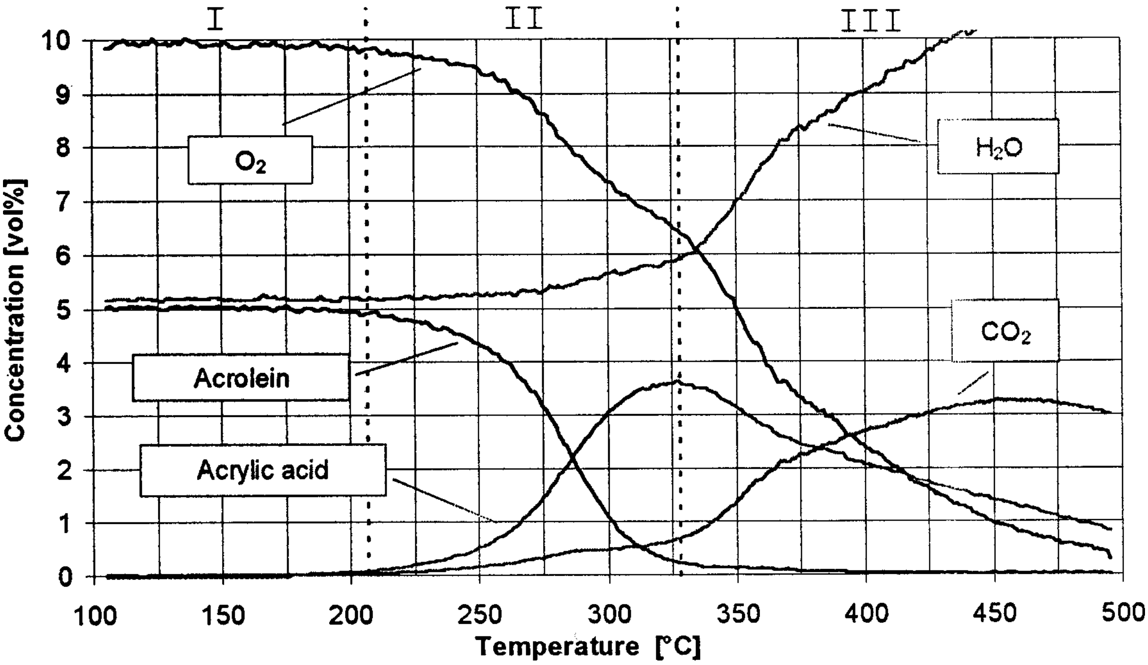

Figure 7. TP reaction spectra for sample 3 (Mo–V–O) with a reactor inlet gas flow whose composition corresponds to typical industrial values. Pretreatment: 60 min with 10 vol% O_2 in N_2 at 350 °C; sample weight: 22 mg; reaction gas: 5 vol% acrolein, 10 vol% O_2, 5 vol% H_2O in N_2; flow rate: 20 ml/min; heating rate: 5 °C/min.

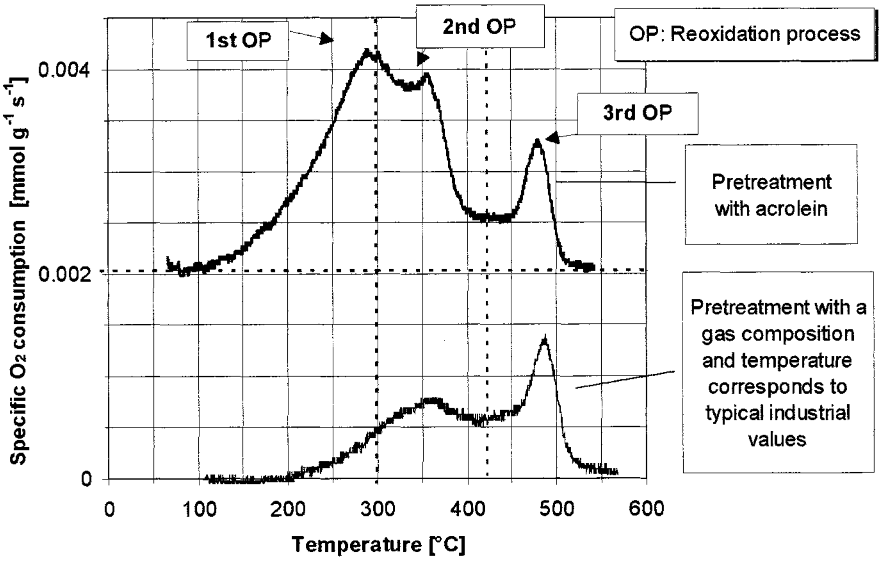

Figure 8. TP oxidation of sample 3 (Mo–V–O) after various pretreatments. Pretreatment: upper curve: 60 min with 10 vol% acrolein in N_2 at 290 °C, lower curve: 9 h with 5 vol% acrolein, 10 vol% O_2, 5 vol% H_2O in N_2 at 290 °C; sample weight: 100 mg; oxidation gas stream: 5 vol% O_2 in He; flow rate: 36 ml/min; heating rate: 10 °C/min. The broken line is the zero line for the upper curve.

trial plant conditions, they are not re-oxidized by the second oxidation process. The results also support the hypothesis of a high oxidation state of the reduction–oxidation cycle that is active under steady-state conditions between the second reduction and first oxidation processes.

4. Derived model for the catalyst's mode of action

A model concept was derived from the previously obtained results. According to this model, the surface of an Mo–V mixed oxide contains various centres Z_i ($i = \alpha, \beta, \gamma, \omega$), which can be assigned to the reduction and oxidation processes characterized by the TP and CP measurements. A diagram of the model is given in figure 9 and then explained in the following text.

Centre Z_α causes the second reduction process at 280–300 °C and the first oxidation process at 300 °C. It determines the catalytic process under industrial plant conditions [4], characterized by highly selective formation of acrylic acid. Centre Z_β, on the other hand, is responsi-

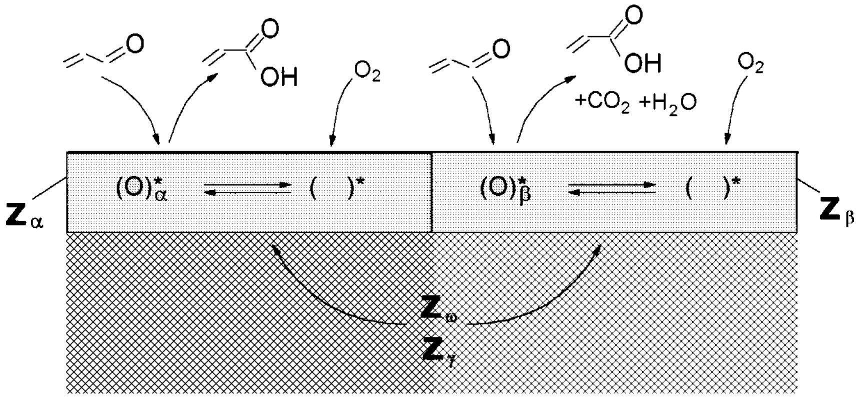

Figure 9. Model of partial oxidation of acrolein catalysed by an Mo–V mixed oxide. Z_i ($i = \alpha, \beta, \gamma, \omega$): active centres.

ble for the first reduction process at 230 °C and the second oxidation process at 350 °C. Z_β already forms acrylic acid "selectively" at temperatures below those of industrial plant conditions, and does so until the oxygen capacity of this centre is exhausted. At temperatures higher than those of industrial conditions, this centre is oxidized. At these higher temperatures, because of its strong oxidizing effect, it can further oxidize acrylic acid to total-oxidation products. Below the "oxidation temperature range" of centre Z_β, centre Z_α dominates the catalytic process. Centres Z_α and Z_β are both on the catalyst surface.

However, the acrylic acid formed during the TP reduction measurements (no oxygen supplied from the gas phase) indicated that bulk oxides must also be involved, for which additional centres (Z_γ and Z_ω) were postulated in the model. Z_γ already supplies lattice oxygen to centres Z_β and Z_α at temperatures <200 °C. This centre is responsible for most of the active oxygen that selectively forms acrylic acid during TP reduction reactions with acrolein in the 200–300 °C temperature range. Mechanistic concepts for the release of oxygen from these bulk oxide species were proposed by Werner et al. [2]. They postulate that lattice oxygen is liberated when two polyhedra linked at a pair of vertices "fold together" to form an edge-linked unit. This process requires considerably less activation than, for example, "shearing" of entire polyhedron planes. Such shearing is assumed, for instance, with bismuthmolybdates used for the oxidation of propene.

The oxidation-active oxygen released from centre Z_ω at temperatures exceeding 400 °C is probably produced by shearing of the structure. It represents the largest amount of oxidation-active oxygen in the lattice. However, at these high temperatures, the liberated oxygen acts as an unselective oxidizing agent. Comparison of the amorphous and crystalline samples in figure 2 shows that the crystalline samples also have Z_ω centres.

5. Conclusions

It was possible to show that non-steady-state reaction methods could be used to identify the individual oxidation centres and characterize their activity/selectivity properties. In steady-state experiments, on the other hand, it is only possible to carry out averaging measurements over all the individual processes at once, because of the simultaneous interaction of the elementary steps. In contrast to this, non-steady-state reaction methods provide additional, differentiated information, by means of which the effect of morphology, and the influence of production and process parameters on individual selective and total-oxidation processes can be elucidated directly. This allows catalyst design to be focused on specific objectives.

Acknowledgement

This work was financially supported by the BMBF through its catalysis programme. We are indebted to the members of the collaborating groups of Professors Gaube, Linz and Schlögl for numerous discussions.

References

[1] P. Mars and D.W. van Krevelen, Spec. Supp. Chem. Eng. Sci. 3 (1954) 41.
[2] H. Werner, O. Timpe, D. Herein, Y. Uchida, N. Pfänder, U. Wild and R. Schlögl, Catal. Lett. 44 (1997) 153.
[3] R. Böhling, A. Drochner, M. Fehlings, D. König and H. Vogel, Chem. Ing. Techn. 71 (1999) 226.
[4] R. Krabbetz, W. Ferrmann, H. Engelbach and P. Balm (BASF AG), Eur. Patent Appl. 0017000 A1 (1980).
[5] R. Böhling, Dissertation (D17), TU Darmstadt (1997).
[6] T.V. Andrushkevich, Catal. Rev. Sci. Eng. 35 (1993) 213.
[7] A.M. Chippindale and A.K. Cheetham, Stud. Inorg. Chem. 19 (1994) 146.