

DOI: 10.1002/cctc.201400099

The Effect of Water on the Heterogeneously Catalyzed Selective Oxidation of Acrolein: An Isotope Study

Tina Petzold, Nina Blickhan, Alfons Drochner, and Herbert Vogel^{*[a]}*Dedicated to Professor Robert Schlögl on the occasion of his 60th birthday*

The effect of water on the selective gas phase oxidation of acrolein to acrylic acid on a Mo/V/W mixed oxide catalyst was studied by performing steady-state isotopic transient kinetic analysis experiments with H₂¹⁸O. Experiments were performed in the temperature range of 90–345 °C at ambient pressure. It could be shown that acrolein exchanges its carbonylic oxygen

with oxygen from water even at low temperatures (< 200 °C), at which no acrolein oxidation occurs. At higher temperatures (> 200 °C), the oxygen atoms of the water molecules incorporate into all oxidation products such as acrylic acid, carbon monoxide, and carbon dioxide.

Introduction

Acrylic acid is produced from propylene in a two-step process, with an annual production of more than 4 million tons.^[1] Mixed oxides such as Mo/V/W oxides are used as catalysts in the second reaction step. Their composition is empirically determined and found to be complex. Many attempts have been made to understand the mechanism of the partial oxidation of acrolein with molecular oxygen as well as the role and cooperation of different metal components. However, for an entire understanding of the mechanism, additional aspects have to be considered: one is the effect of water, which is a natural by-product in the industrial process and affects the mechanism of acrolein oxidation significantly.

The effect of water on the structure and performance of mixed oxide catalysts has been studied earlier. In the presence of additionally fed water, both the conversion and the selectivity towards acrylic acid are increased. The addition of 7.5 vol% of water leads to a much higher conversion at lower temperatures. A selectivity of more than 90% is achieved at 80% conversion.^[2]

In general, the effect of water on oxidic systems is discussed in the literature:

- 1) Physical effects are discussed, such as the improvement in heat removal.^[3]
- 2) Water prevents coke formation; more active sites are available.^[4]
- 3) Water accelerates the re-oxidation of the catalyst.^[5,6]
- 4) Water increases the active sites of the catalyst.^[7,8]

- 5) The desorption of acrylic acid is promoted in the presence of water; therefore, the total oxidation of acrylic acid is reduced.^[9–12]
- 6) Water increases the adsorption sites on the catalyst surface; therefore, more acrolein can be adsorbed on the catalyst surface.^[13–16]

To obtain more mechanistic information, isotopic investigations are required. Only a few experiments, performed under reaction conditions, with H₂¹⁸O on oxidic catalyst systems are mentioned in the literature.

For example, Suprun et al. investigated the oxidation of 1-butene to acetic acid on the VO_x-TiO₂ system. The conclusions drawn from this study confirm the assumption that water promotes the desorption of the partial oxidation product on the catalyst surface. Acetic acid is probably chemically bonded to the catalyst surface as an acetate species; water hydrolyses the acetate to the free acid. There is evidence that water has an active role in the reaction mechanism because the oxygen atom from the water molecule incorporates into the oxidation products faster than does the molecular oxygen from the gas phase.^[12]

The aim of our study was to clarify the role of water in the selective oxidation of acrolein to acrylic acid on Mo/V/W mixed oxides. The effect of water on the selective oxidation on these mixed oxides was investigated by performing temperature-programmed experiments. We also performed isotope exchange [steady-state isotopic transient kinetic analysis (SSITKA)] experiments with H₂¹⁸O at several temperatures to follow the reaction pathway of the oxygen originating from water into educts and oxidation products. Herein, a Mo/V/W mixed oxide was used, which shows up to 70% selectivity at 80% conversion.^[17,18]

[a] T. Petzold, N. Blickhan, Prof. Dr. A. Drochner, Prof. Dr. H. Vogel
Ernst-Berl-Institut für Technische und Makromolekulare Chemie
Technische Universität Darmstadt
Alarich-Weiss-Straße 8, 64287 Darmstadt (Germany)
Fax: (+49) 6151-16-3465
E-mail: vogel@ct.chemie.tu-darmstadt.de

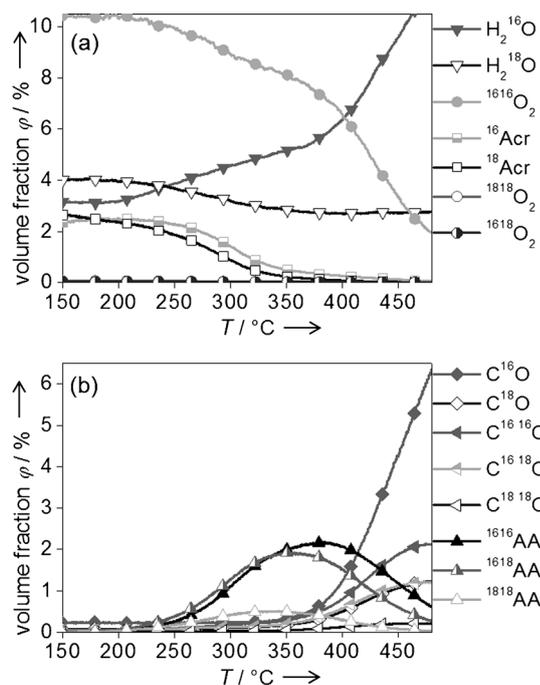


Figure 1. Concentration profiles of the temperature-programmed reaction experiment: a) acrolein, oxygen, and water; b) acrylic acid, carbon monoxide, and carbon dioxide. Feed: 5 vol% acrolein, 10 vol% oxygen, and 7.5 vol% H_2^{18}O ; heating rate: 10 K min^{-1} .

Results and Discussion

Temperature-programmed reaction experiment with H_2^{18}O

The concentration profiles of the educts and products obtained during a temperature-programmed reaction experiment with H_2^{18}O are shown in Figure 1. The concentration profiles of the educts acrolein, oxygen, and water are shown in Figure 1a. Surprisingly, ^{18}O -labelled acrolein could be detected even at temperatures below 200 °C, at which no oxidation occurs. In addition, the formation of H_2^{16}O could be verified, which indicates that water and acrolein can exchange their oxygen atoms. H_2^{16}O could be formed through an exchange reaction between H_2^{18}O and ^{16}Acr . Below 200 °C, this is the only possible way to form H_2^{16}O . At higher temperatures, H_2^{16}O could also be formed by the combustion of acrolein or acrylic acid with the start of the oxidation reactions. In addition to the exchange reaction between water and acrolein, an oxygen exchange between H_2^{18}O and ^{16}O -labelled acrylic acid can occur at higher temperatures. $^{1618}\text{O}_2$ and $^{1818}\text{O}_2$ could not be detected. This finding leads to the conclusion that once gas phase oxygen incorporates into the catalyst, there is no recombination of the oxygen atoms (within the resolution of the used online mass spectrometer).

However, all three isotopologues of acrylic acid (^{1616}AA , ^{1618}AA , and ^{1818}AA) are formed. Their maxima appear at different temperatures (^{1616}AA : 375 °C; ^{1618}AA : 350 °C; ^{1818}AA : 325 °C). The sum of all acrylic acid species corresponds to the acrylic acid concentration of a temperature-programmed reaction experiment with the similar amount of H_2^{16}O in the feed. Hence, no kinetic isotope effect could be evaluated.

All isotopologues of the combustion products (carbon monoxide and carbon dioxide) are formed in a similar manner.

The next question is whether the oxygen exchange between water and acrolein occurs only on the catalyst or even in the gas phase. For this purpose, a blind experiment (SSITKA experiment) without any catalyst was performed, which is described below (Figure 3).

SSITKA experiments with $\text{H}_2^{16}\text{O}/\text{H}_2^{18}\text{O}$

Concentration profiles

SSITKA experiments with H_2^{18}O were performed in a temperature range of 90–345 °C. By using this method, it is possible to follow the reaction pathway of the oxygen atom from water. Under steady-state conditions at 90 °C, H_2^{16}O was replaced stepwise by H_2^{18}O (Figure 2). The resulting concentration pro-

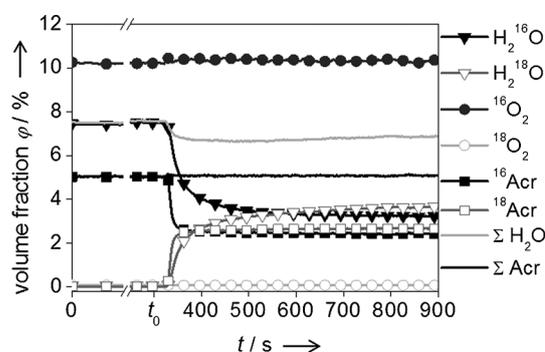


Figure 2. SSITKA experiment with H_2^{18}O at 90 °C. Transient responses of acrolein, oxygen, and water after the stepwise change from H_2^{16}O to H_2^{18}O in the feed gas at $t = t_0$ (5 vol% acrolein, 10 vol% oxygen, 7.5 vol% water in helium, 50 mg of $\text{Mo}_8\text{V}_2\text{W}_{15}\text{O}_x$).

files reveal that acrolein exchanges more than 50% of its carbonyl oxygen with ^{18}O -labelled oxygen from water. During these experiments, the concentration of the molecular oxygen from the gas phase remains constant. This finding confirms the overall steady state of the experiment and that no exchange between molecular oxygen from the gas phase and oxygen from water or acrolein occurs.

To ensure that this effect is due to the presence of the catalyst, a reference measurement without any catalyst was performed (Figure 3). At 160 °C, acrolein can exchange 40% of its oxygen with oxygen from water (Figure 3a). In contrast, the reference measurement without any catalyst indicates that no labelled acrolein appears (Figure 3b). This observation reveals that the exchange of oxygen occurs only on the catalyst surface (Scheme 1). The gas phase oxygen does not participate directly in the exchange reaction.



Scheme 1. Illustration of the oxygen exchange between water and acrolein.

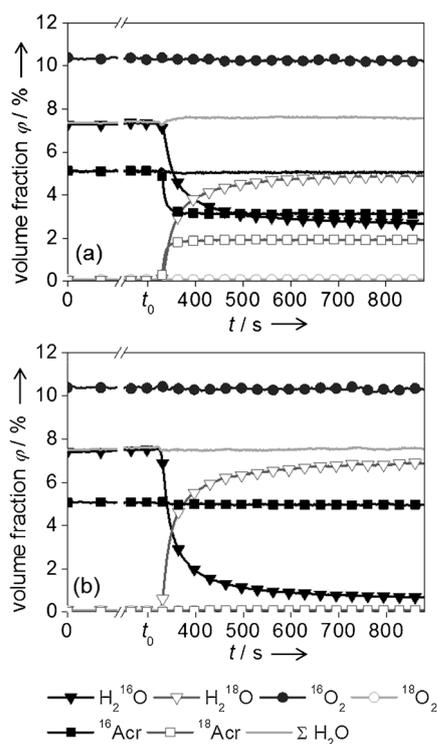


Figure 3. SSITKA experiment with H_2^{18}O at 160°C . Transient responses of acrolein, oxygen, and water after the stepwise change from H_2^{16}O to H_2^{18}O in the feed gas at $t=t_0$. a) Exchange on the catalyst. b) Exchange in an empty reactor (5 vol% acrolein, 10 vol% oxygen, 7.5 vol% water in helium, 50 mg of $\text{Mo}_8\text{V}_2\text{W}_{13}\text{O}_x$).

To investigate this oxygen exchange under reaction conditions, we performed a SSITKA experiment at 270°C . The response of the system after the exchange from H_2^{16}O to H_2^{18}O is shown in Figure 4. Again, the concentration of oxygen remains constant during the experiment. At this temperature, acrolein converts to acrylic acid and combustion products. In this regard, the conversion is approximately 44%. The labelled oxygen of water appears in every product, as shown in Figure 4a–c. For both acrylic acid and carbon dioxide, mixed labelled and fully substituted isotopologues were detected. The concentration of the mixed labelled species is always higher than that of the fully substituted species.

Degree of labelling

Firstly, the degree of labelling of the reactants during a SSITKA experiment with H_2^{18}O is discussed for the temperatures at which no reaction occurs (measurements at 90, 120, and 160°C). Here, we observe an interaction only between acrolein, water, and the catalyst. Then, the degree of labelling of all reactants is discussed for the entire temperature range.

The degree of labelling of the individual components is calculated by using the volume fraction φ (Table 1).

The temperature-dependent degree of labelling of acrolein and water 10 min after switching from H_2^{16}O to H_2^{18}O is depicted in Figure 5. Up to 160°C , no acrolein oxidation occurs and the interaction between water and acrolein can be described

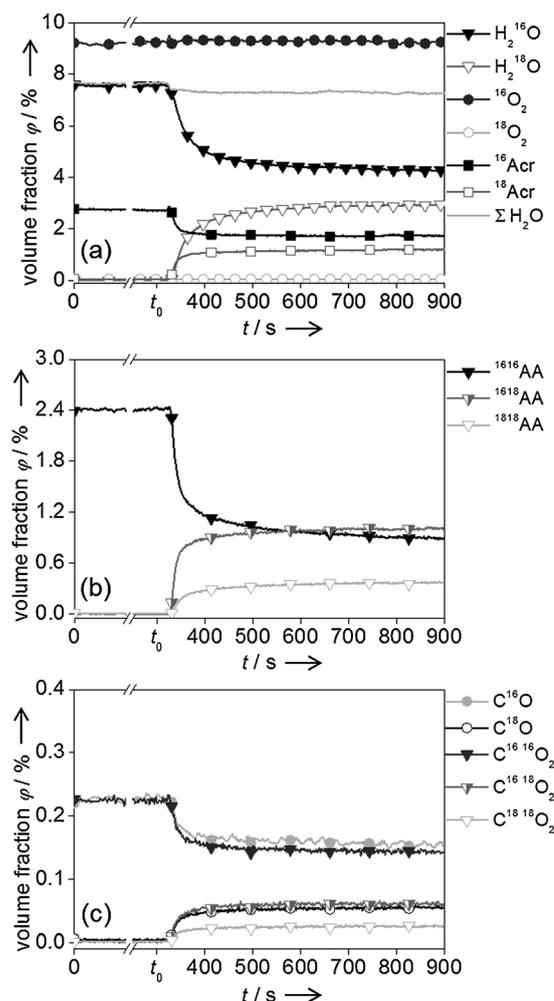


Figure 4. SSITKA experiment with H_2^{18}O at 270°C . Transient responses of a) acrolein, oxygen, and water, b) acrylic acid, and c) carbon monoxide and carbon dioxide after the stepwise change from H_2^{16}O to H_2^{18}O in the feed gas at $t=t_0$ (5 vol% acrolein, 10 vol% oxygen, 7.5 vol% water in helium, 50 mg of $\text{Mo}_8\text{V}_2\text{W}_{13}\text{O}_x$).

Table 1. Degree of labelling of acrolein, acrylic acid, carbon dioxide, carbon monoxide, and water.

Component	Degree of labelling, η
Acrolein	$\eta_{Acr} = \frac{\varphi^{18}_{Acr}}{\varphi^{16}_{Acr} + \varphi^{18}_{Acr}}$
Acrylic acid	$\eta_{AA} = \frac{2\varphi^{1818}_{AA} + \varphi^{1618}_{AA}}{2(\varphi^{1616}_{AA} + \varphi^{1618}_{AA} + \varphi^{1818}_{AA})}$
Carbon dioxide	$\eta_{CO_2} = \frac{2\varphi^{1818}_{CO_2} + \varphi^{1618}_{CO_2}}{2(\varphi^{1616}_{CO_2} + \varphi^{1618}_{CO_2} + \varphi^{1818}_{CO_2})}$
Carbon monoxide	$\eta_{CO} = \frac{\varphi^{18}_{CO}}{\varphi^{16}_{CO} + \varphi^{18}_{CO}}$
Water	$\eta_{H_2O} = \frac{\varphi^{18}_{H_2O}}{\varphi^{16}_{H_2O} + \varphi^{18}_{H_2O}}$

without superposition of the oxidation reaction. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) investigations on a similar catalyst^[19] reveal that the band intensities of the hydroxyl groups on the catalyst surface decreases with

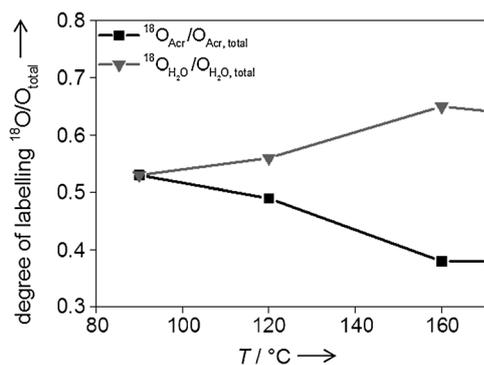


Figure 5. Degree of labelling of acrolein and water versus temperature (after 10 min in the presence of 5 vol% acrolein, 10 vol% oxygen, and 7.5 vol% H_2^{18}O).

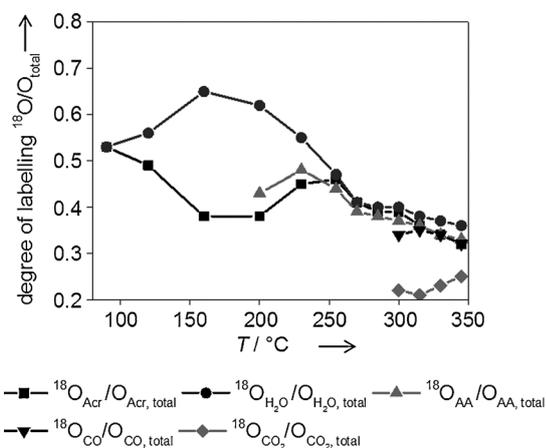


Figure 6. Degree of labelling after 10 min in the presence of 7.5 vol% H_2^{18}O , 5 vol% acrolein, and 10 vol% oxygen at 12 temperatures.

increasing temperature. This is most likely the explanation for the decreasing degree of labelling of acrolein. With increasing temperature, the number of labelled hydroxyl groups on the catalyst surface decreases and acrolein has therefore less possibility to exchange its carbonyl oxygen.

The oxidation reaction starts at temperatures above 160°C , and the degree of labelling of acrolein increases with increasing activity (Figure 6). With increasing conversion, more gas phase $^{16}\text{O}_2$ takes part in the reaction. The catalyst is re-oxidized with unlabelled oxygen from the gas phase. Hence, this oxygen is available for exchange with oxygen from acrolein and thus incorporates into all oxidation products. Thus, the degree of labelling of acrolein decreases with increasing conversion. As a result, the degree of labelling of water decreases above 160°C . At 250°C and above, the degree of labelling of acrolein, acrylic acid, and water is identical.

The degree of labelling of carbon monoxide and carbon dioxide is plotted only in the temperature range $300\text{--}345^\circ\text{C}$. Below 300°C , the concentrations of these components are too small to give reliable values.

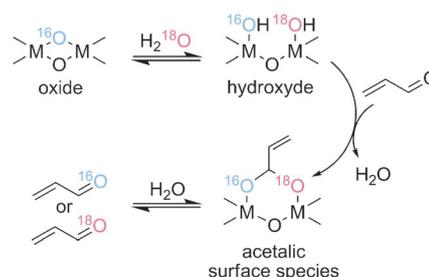
The degree of labelling of carbon monoxide decreases with increasing temperature and has the same isotopic distribution

as acrylic acid, acrolein, and water above 315°C . In contrast, the degree of labelling of carbon dioxide increases with increasing temperatures. This difference between carbon monoxide and carbon dioxide is an indicator of different formation pathways.

Conclusions

The results of steady-state isotopic transient kinetic analysis experiments with H_2^{18}O on $\text{Mo}_8\text{V}_2\text{W}_{1.5}\text{O}_x$ indicate the participation of water in the acrolein partial oxidation reaction. At low temperatures (90°C), a fast oxygen exchange between water and acrolein occurs. Under the chosen conditions, more than 50% of acrolein exchanges its carbonyl oxygen with ^{18}O -labelled oxygen from water. This exchange occurs only on the catalyst surface. Without any catalyst, no exchange reaction occurs. Regarding the degree of labelling, the situation changes at temperatures above 160°C , at which acrolein is converted to acrylic acid and combustion products.

The labelled oxygen is recovered in every oxidation product owing to the oxygen exchange between acrolein and water (Scheme 2).



Scheme 2. Illustration of the incorporation of oxygen originating from H_2^{18}O into acrolein.

The formation of double-labelled acrylic acid involves different pathways. Owing to the adsorption and desorption of water, ^{18}O -labelled oxygen permanently incorporates into the catalyst ($\text{M-O-M} + \text{H}_2\text{O} \rightleftharpoons 2\text{M-OH}$). The adsorption and desorption of acrolein on labelled hydroxyl groups results in labelled acrolein. The next step towards the formation of acrylic acid is the incorporation of oxygen. Therefore, the degree of labelling of acrylic acid depends on the oxygen isotope (^{16}O or ^{18}O), which incorporates into the acrolein surface complex. ^{1616}AA or ^{1618}AA could be formed on the basis of ^{16}Acr and ^{1618}AA , and ^{1818}AA could be formed on the basis of ^{18}Acr . Without doubt, the formation of ^{1818}AA could also proceed via an adsorption and desorption equilibrium of acrylic acid and labelled hydroxyl groups (formal reaction: $\text{H}_2^{18}\text{O} + ^{1618}\text{AA} \rightleftharpoons \text{H}_2^{16}\text{O} + ^{1818}\text{AA}$). Another way to form double-labelled acrylic acid was discovered earlier. In previous works, we could show through $^{18}\text{O}_2$ -SSITKA experiments with ^{1616}AA that in addition to the combustion reaction the formation of ^{1618}AA and ^{1818}AA occurs,^[20–22] which could only be due to an oxygen exchange between acrylic acid and the catalyst surface. If there was no exchange, only a stationary trend of ^{1616}AA would be expected regarding the

results of SSITKA experiments with $^{18}\text{O}_2$. The molecular oxygen from the gas phase does not exchange directly its oxygen atoms with those from water or any other component.

The variation in temperature leads to the conclusion that the degree of labelling of acrolein depends on the concentration of the hydroxyl groups on the catalyst surface. Lower temperatures lead to a higher hydroxyl group density on the surface.^[19] Therefore, an increased oxygen exchange with oxygen from acrolein occurs. In contrast, the surface hydroxyl group density decreases with increasing temperature through dehydration reactions.

In addition, the degree of labelling of all components, except for carbon dioxide, decreases at higher temperatures because with increasing conversion the catalyst re-oxidizes with unlabelled oxygen from the gas phase. This unlabelled oxygen is then available for the exchange with oxygen from acrolein (or acrylic acid). On the one hand, H_2^{18}O forms fewer hydroxyl groups on the surface at higher temperatures and thus acrolein (or acrylic acid) has less opportunity to exchange its oxygen with labelled oxygen from water. On the other hand, more unlabelled oxygen species ($^{16}\text{O}_2$) incorporate into the catalyst through re-oxidation and are exchanged with oxygen from acrolein and incorporate into all oxidation products.

Experimental Section

Catalyst preparation

The catalyst with the general formula $\text{Mo}_8\text{V}_2\text{W}_{1.5}\text{O}_x$ ($23 \leq x \leq 33.5$) was prepared by using the preparation strategy developed by Kunert et al.; details are described in previous works.^[16,18,23,24] An aqueous solution containing ammonium heptamolybdate, ammonium metavanadate, and ammonium metatungstate with the desired metal ratio of the solid catalyst was adjusted to a pH value of 5 and was boiled under reflux for 90 min. The cooled solution was spray dried (600 kPa air, 260 °C). The dried precursor was calcined in nitrogen atmosphere at 325 °C for 4 h.

Reactor apparatus

Isotope exchange experiments were conducted in a setup described elsewhere.^[23,24] An arrangement of several mass flow controllers and two-stage gas saturators allowed a flexible dosage of gaseous and liquid components. A quartz U tube 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 analyzed online with a mass spectrometer (GAM 400, InProcess Instruments, Germany).

A prerequisite for a SSITKA experiment with H_2^{18}O was a nearly ideal switch between H_2^{16}O and H_2^{18}O without disturbing the overall flow. A syringe pump was used for this purpose. It consisted of a step motor driving a screw that moved two plungers simultaneously into two cylinders: one was filled with water (H_2^{16}O) and the other one with ^{18}O -labelled water (H_2^{18}O). With use of a heating block system, water was continuously evaporated and was carried to the feed with inert gas.

Temperature-programmed reaction experiments

Temperature-programmed reaction experiments were conducted with H_2^{18}O in the feed to evaluate the effect of water on the performance of mixed oxides in dependence on temperature.

The calcined catalyst was pretreated in the reactor in an oxidative atmosphere (400 °C, 60 min, flow rate: 20 mL min⁻¹, 10 vol% oxygen in helium). Subsequently, three consecutive temperature-programmed reaction cycles were performed (heating rate: 10 K min⁻¹, final temperature: 480 °C). The feed consisted of acrolein (5 vol%), oxygen (10 vol%), and water (7.5 vol%). Each temperature-programmed reaction cycle was followed by a re-oxidation process (10 vol% oxygen at 400 °C for 60 min). By repeating this method, we could assess the activation and deactivation processes as well as the long-term stability of the catalyst under thermal stress.

SSITKA experiments

Isotope exchange experiments were performed to obtain information about the oxygen dynamics. The technique involved the replacement of a reactant by one of its isotopologues in the gas flow (here H_2^{16}O against H_2^{18}O), but the overall reaction remained at steady state.

To abbreviate the start-up phase of the catalyst system under reaction conditions, a pretreatment was performed as follows: A 1 h treatment (10 vol% oxygen, 400 °C) followed by two temperature-programmed reaction cycles (10 vol% oxygen, 5 vol% acrolein, 7.5 vol% water, heating rate: 10 K min⁻¹) and consecutive re-oxidation of the catalyst (30 min, 400 °C, 10 vol% oxygen) were performed.

All experiments were performed under the continuous flow of the reaction gas mixture (5 vol% acrolein, 10 vol% oxygen, 7.5 vol% water, flow rate: 20 mL min⁻¹). Under steady-state conditions, after setting the target value to the appropriate temperature the switch to H_2^{18}O (> 97%, Sigma-Aldrich) occurred. After another 10 min, H_2^{18}O was switched back to H_2^{16}O .

The response of the system after the water exchange was monitored, and the rate of oxygen exchange and the isotopic distribution of all components were analyzed. Measurements were performed at 12 temperatures ranging from 90 to 345 °C.

Keywords: acrolein · heterogeneous catalysis · mixed oxides · oxidation · isotopic exchange

- [1] *Ullmann's Encyclopedia of industrial chemistry*, 7th ed., Wiley-VCH, Weinheim, 2009.
- [2] T. Jekewitz, A. Drochner, H. Vogel, *Catal. Commun.* **2012**, 20, 25–28.
- [3] H.-J. Arpe, *Industrielle Organische Chemie*, 6th ed., Wiley-VCH, Weinheim, 2007.
- [4] J.-S. Yu, L. Kevan, *J. Phys. Chem.* **1991**, 95, 6648–6653.
- [5] H. Redlingshöfer, O. Kröcher, W. Böck, K. Huthmacher, G. Emig, *Ind. Eng. Chem. Res.* **2002**, 41, 1445–1453.
- [6] L. B. Levy, P. B. DeGroot, *J. Catal.* **1982**, 76, 385–392.
- [7] R. Recknagel, L. Riekert, *Chem. Tech.* **1994**, 46, 324–331.
- [8] E. K. Novakova, E. G. Derouane, J. C. Vadrine, *Catal. Lett.* **2002**, 83, 177–182.
- [9] T. V. Andrushkevich, *Catal. Rev. Sci. Eng.* **1993**, 35, 213–259.
- [10] E. M. Erenburg, T. V. Andrushkevich, G. Y. Popova, A. A. Davydov, V. M. Bondareva, *React. Kinet. Catal. Lett.* **1979**, 12, 5–11.
- [11] Y. A. Saleh-Alhamed, R. R. Hudgins, P. L. Silveston, *J. Catal.* **1996**, 161, 430–440.
- [12] W. Y. Suprun, D. P. Sabde, H.-K. Schädlich, B. Kubias, H. Papp, *Appl. Catal. A* **2005**, 289, 66–73.

- [13] J. Tichý, A. A. Davydov, *Collect. Czech. Chem. Commun.* **1976**, *41*, 834–838.
- [14] J. Tichý, J. Svachula, J. Machek, N. C. Allachverdova, *React. Kinet. Catal. Lett.* **1986**, *31*, 159–166.
- [15] M. M. Bettahar, G. Costentin, L. Savary, J. C. Lavalley, *Appl. Catal. A* **1996**, *145*, 1–48.
- [16] J. Kunert, A. Drochner, J. Ott, H. Vogel, H. Fueß, *Appl. Catal. A* **2004**, *269*, 53–61.
- [17] S. Endres, P. Kampe, J. Kunert, A. Drochner, H. Vogel, *Appl. Catal. A* **2007**, *325*, 237–243.
- [18] P. Kampe, L. Giebeler, D. Samuelis, J. Kunert, A. Drochner, F. Haaß, A. H. Adams, J. Ott, S. Endres, G. Schimanke, T. Buhrmester, M. Martin, H. Fuess, H. Vogel, *Phys. Chem. Chem. Phys.* **2007**, *9*, 3577–3589.
- [19] K. Krauß, A. Drochner, M. Fehlings, J. Kunert, H. Vogel, *J. Mol. Catal. A* **2000**, *162*, 413–422.
- [20] P. Kampe, *Dissertation*, Technische Universität Darmstadt, **2007**.
- [21] A. Drochner, P. Kampe, N. Blickhan, T. Jekewitz, H. Vogel, *Chem. Ing. Tech.* **2011**, *83*, 1667–1680.
- [22] A. Drochner, P. Kampe, N. Menning, N. Blickhan, T. Jekewitz, H. Vogel, *Chem. Eng. Technol.* **2014**, *37*, 398–408.
- [23] A. Drochner, P. Kampe, J. Kunert, J. Ott, H. Vogel, *Appl. Catal. A* **2005**, *289*, 74–83.
- [24] R. Böhling, A. Drochner, M. Fehlings, D. König, H. Vogel, *Chem. Ing. Tech.* **1999**, *71*, 226–230.

Received: January 30, 2014

Revised: March 25, 2014

Published online on May 30, 2014