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Short Communication

The influence of water on the selective oxidation of acrolein to acrylic acid on Mo/V/W-mixed oxides

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ABSTRACT

The influence of water on the selective gas phase oxidation of acrolein to acrylic acid on Mo/V/W-mixed oxides was investigated by means of temperature-programmed experiments. In the presence of water, the rate of the acrylic acid formation is significantly pronounced. Selectivity- and yield-maxima are broadened and shifted towards lower temperatures. Nonetheless, the combustion remains unaffected. Furthermore, the catalysts stability remains likewise unaffected within the range of the experiments.

1. Introduction

Acrylic acid (AA) and its esters are important bulk chemicals with a broad application in the polymer industry, for example as superabsorbers, fabrics, adhesives and paints. The global annual production of crude AA is about 4 million tons, mostly based on the two-step propene oxidation process [1,2]. In the first step, propene is selectively oxidised with air on Bi/Mo-catalysts to acrolein (ACR). As a result of the partial oxidation to ACR water is formed as a coproduct. Subsequently, ACR, water and additional air are fed into the second step without further purification. The catalysts here are based on Mo/V/W-mixed oxides to convert ACR to AA [1,2]. Much is known about the propene oxidation to ACR, however, only little is known in detail about the mechanistic understanding of the selective oxidation of ACR to AA. Therefore, the object of our work is to focus on the catalytic system of the second step. Water vapour shifts the explosion limits and has a high heat capacity (ca. 36 J mol^{-1} K^{-1} compared to nitrogen with ca. 27 J mol^{-1} K^{-1}) by what it serves as an inert mass to reduce hot-spots. In this way water induces a higher selectivity, reduces the formation of coke layer and decelerates the catalyst deactivation [2]. However, a physical reason doesn't explain the gain in performance satisfactorily. Obviously water participates in the reaction mechanism. In general the understanding of the role of water suffers from the incomplete knowledge about heterogeneously catalysed oxidation reactions.

For this reason, only some mechanisms are discussed in literature to describe the influence of water on different partial oxidations. However, some basic motives recur:

- One often mentioned reason for the higher selectivity in partial oxidation reactions is a competing adsorption of water between originated oxygenates leading to a faster desorption of those from the catalyst surface. From this it follows that the consecutive total oxidation is repressed [9–14].
- The addition of water results in the formation of hydroxyl groups on the catalysts surface. The metal oxide catalyst offers a great number of Lewis-acid centres. Water adsorbs on those and forms Broensted-acid centres. These serve as electrophilic centres for the partial oxidation [3,6–8]. Landi et al. have found a linear dependency between the AA-formation rate and the number of acid groups on the catalysts surface [5].
- Some authors report a higher crystallinity after the treatment with water vapour. Landi et al. activated V/P/O-catalysts in a water-containing feed. In comparison, catalysts treated in this way show a higher selectivity and more intense peaks in XRD [4,5]. Others like Levy et al. found faster recrystallisation accompanied by a decreasing performance in the presence of water [20].
- Böhling et al. postulate, that the active phase needs to be in a certain reduction state [27]. Guliants et al. share this perception and suppose that water may support and maintain this reduction degree [3]. Levy et al. investigated the deactivation process of mixed oxides and found a correlation between an overoxidation of the catalyst and the deactivation by recrystallisation, which was accelerated in the presence of water. From this they conclude that the oxidation of the

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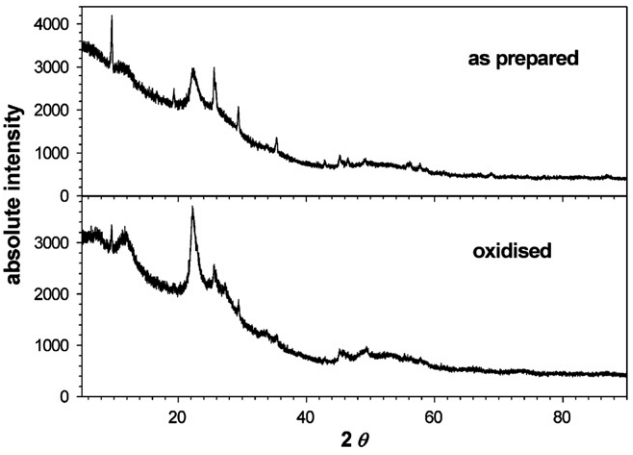

Fig. 1. XRD-pattern of the spray-dried (as prepared) and oxidative pre-treated (oxidised) catalyst $Mo_8V_2W_{1,5}O_x$.

catalyst is faster in presence of water. They postulate a mechanism which not only shows how hydroxyl groups built on the catalysts surface accelerate the reoxidation but also explains the exchange of oxygen between the catalyst and water [20]. This process was likewise observed by measurements with $H_2^{18}O$ by Novakova et al. [21].

- On the other hand several working groups describe an acceleration of the reoxidation instead [17,18]. Suprun et al. found that in isotope exchange experiments labelled oxygen is incorporated faster into the oxidation products in the presence of water. He observed that oxygen from water is incorporated into the products even faster than molecular oxygen [19].
- The influence of water on the oxidation of ACR on the catalyst is discussed controversially. Tichy et al. found a deceleration of the reoxidation process in the presence of water by measuring of the V^{4+}-species in dependence of time under an oxygen atmosphere in both the presence and absence of water [16].
- Saleh-Alhamed et al. investigated the influence of water on the partial oxidation of propene over Sb/Sn/V-catalysts. TPD experiments performed after loading the catalyst with AA, with water and then again with AA, show that the surface – if pre-treated with water – cannot adsorb as much AA as without such a pre-treatment. Isotope exchange experiments with $^{18}O_2$ on the same system show a faster relaxation of the transients in the presence of water. Water blocks the CO_2-formation sites and enhances the catalytic oxidation by keeping the surface at a high oxidation state. Furthermore, isotope exchange experiments with $^{18}O_2$ in presence of H_2O show an oxygen exchange between water and the catalyst surface [15].
- There are mechanisms describing the heterogeneously catalysed partial oxidation of ACR as well, but a mechanism of ACR oxidation taking into account the participation of water still has to be developed [22,23].

The main objective of this work is to gain more information about the influence of water on the partial oxidation of ACR. In this context results obtained by TP-reaction experiments with various water concentrations will be given.

2. Experimental

2.1. Catalyst

Catalysts with the general formula $Mo_8V_2W_{1,5}O_x$ were prepared, following the preparation method developed by Kunert et al. [24]. Details have already been described in previous works [23,25,28]. An aqueous solution containing ammonium heptamolybdate, -metavanadate and -metatungstate according to the desired metal ratio of the solid catalyst was adjusted to pH 5 and boiled under reflux for 90 min. The solution was spray-dried in a laboratory spray-dryer, atomised with 6 bar compressed air at 260 °C. The dried precursor was subjected to a calcination procedure under nitrogen atmosphere at 325 °C over a period of 240 min.

2.2. Experimental setup

XRD-measurements have been performed with a STOE powder diffraction system (StadiP, Stoe & Cie, flat specimen holder, transmission geometry, Ge[111]-monochromator, 1.5406 Å, Detector Dectris Mythen 1 K).

Temperature-programmed reactions were conducted in a kinetic-apparatus equipped with a tubular reactor. The whole setup has been previously described elsewhere [26,27]. An arrangement of mass flow controllers and two stage gas saturators allows a flexible dosage of gaseous and liquid components such as ACR and AA. A quartz U-tube (inner diameter 4 mm) serves as reactor in which the catalyst is fixed between two stoppers of quartz wool. An electrically heated oven controls the reactor temperature. The reaction gas is continuously analysed by an on-line mass spectrometer (GAM400, InProcess Instruments).

2.3. Measurement procedure

Temperature-programmed reactions (TP-reaction) were conducted in the presence and absence of water in the feed. The influence of water on the performance of the mixed oxides as a function of the

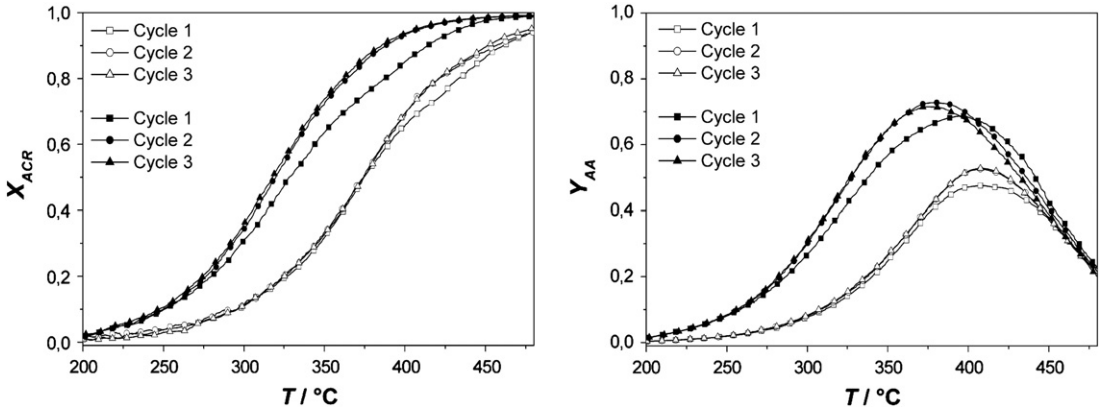

Fig. 2. Conversion of ACR (X_{ACR}) and yield of AA (Y_{AA}) as a function of the reactor temperature. The depicted data represent an entire TP-reaction experiment. Filled symbols represent experiments in the presence of water. Blank symbols represent the results without feeding addition water. Feed: 20 mL min^{-1}, 10 vol.% O_2, 5 vol.% ACR, (7 vol.% H_2O), 10 K min^{-1}, 50 mg $Mo_8V_2W_{1,5}O_x$.