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Activity and selectivity investigations of copper catalysis by concentration programmed reaction method

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ABSTRACT

Copper catalysis proceeds with multiple steady states and oscillations in several oxidation reactions. The understanding of such kinetic phenomena is essential for the control of copper-catalyzed industrial scale processes. Information about the reasons and the ranges of the parameters causing these kinetic effects will be given from results gained by concentration programmed reaction (CP-reaction) experiments. Elemental copper was used as unsupported catalysts and the oxidation of hydrogen and ethanol were introduced as model reactions. CP-reaction experiments were performed in a tubular reactor as well as in a differential thermal gravimetric analyzer (TG/DTA). The application of a TG/DTA as a reactor gave the opportunity for a simultaneous measurement of the activity and the grade of oxidation of the copper catalyst.

1. Introduction

Copper in association with oxygen is an efficient catalyst for the oxidation of alcohols to the corresponding aldehydes. There are two main reaction pathways: the partial oxidation (1) to the corresponding aldehyde and the total oxidation (2):

$$C_nH_{2n+1}OH + 1/2O_2 \rightarrow C_{n-1}H_{2n-1}CHO + H_2O \quad (1)$$

$$C_nH_{2n+1}OH + 3/2nO_2 \rightarrow nCO_2 + (n+1)H_2O \quad (2)$$

Via surface science studies on the oxidation of methanol and ethanol on Cu(1 1 0), Wachs and Madix [1,2] have shown that the copper surface is active when it is in a partially oxidized state. The ability of copper to adsorb alcohols dissociatively was found to be enhanced by the presence of oxygen (oxygen-induced adsorption). The adsorbed nucleophilic oxygen species is able to activate O–H and C–H bonds leading to aldehydes and water formation.

Copper catalysis has been investigated, e.g. for the oxidation of hydrogen [3], the oxidative dehydrogenation of methanol to formaldehyde [4–6] and the oxidation of propylene to acrolein [7]. Remarkably, in all these cases (independent of the chosen reductant) both the activity and selectivity show hysteresis effects under certain reaction conditions. Furthermore, the Cu-catalysis is sometimes accompanied by a strong dynamic behavior. All this is manifested in the occurrence of multiple steady states or non-linear kinetic phenomena like oscillations [8]. These phenomena are caused by the formation of different copper-oxide-phases or different oxygen species on the copper surface, respectively. Additionally, the restructuring of the surface superposed by the redox-behavior of the catalyst bulk emphasizes the complexity of this catalytic system.

The aim of this work is to investigate copper-catalyzed reactions with regard to the multiple steady states and the dynamic behavior, like hysteresis and oscillations. Thus, transient kinetic experiments in the form of CP-reactions were performed at different temperatures on pre-treated elemental copper.

2. Experimental

All experiments were performed under continuous flow (overall volume flow 100 ml min^{-1}, standard conditions) and at ambient pressure. The reaction gas mixtures were balanced with argon. As model reactions the oxidation of hydrogen to water and the partial oxidation of ethanol to acetaldehyde were investigated. Previous to each CP-reaction experiment a pre-treatment was carried out with the intent to reduce the time required to stabilize the catalyst. After pre-treatment, CP-reactions were carried out at constant temperatures in a range between 360 and 440 °C. The experimental set-ups consist of three main parts: a gas dosing unit, the reactor (TG/DTA-apparatus or tubular reactor) and the analytical apparatus. The gas dosing was carried out by mass-flow controllers (Bronkhorst) and two-stage saturators for the addition of the liquid components.

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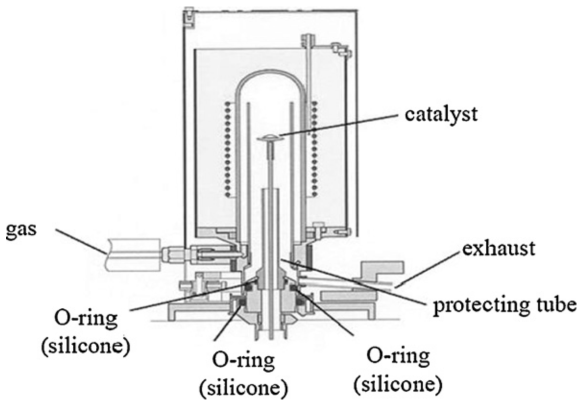

Fig. 1. Schematic drawing of the reactor (TG/DTA-apparatus) for the investigation of the hysteresis in the hydrogen-oxidation via CP-reaction.

2.1. *TG/DTA-analyzer*

A differential thermal gravimetric analyzer (Netzsch, STA 449 C, see Fig. 1) was used as a reactor to investigate the oxidation of hydrogen on copper. The mass changes (TG-signal) as well as the activity (DTA-signal) of the Cu-catalysts could be measured during the experiments. A 7.5 mg portion of the sample was placed in an aluminum crucible (5 mm diameter, 2.5 mm depth), which was set on the sample holder.

2.2. *Tubular reactor*

The partial oxidation of ethanol was performed in a U-tube reactor (inner diameter 4 mm) consisting of quartz glass in which the catalyst (7.5 mg) is fixed between two quartz wool plugs (Fig. 2). On-line analysis of the gaseous components at the reactor outlet has been performed by a quadrupole mass spectrometer (InProcess Instruments, GAM 400). Before the actual measurement an extensive calibration with each component has been carried out. The calibration itself is based on a complex matrix involving the dependencies between the ion currents and the gas concentrations as well as the fact that some components have peaks at the same mass number. All this is implemented in a software routine. However, the application of such a calibration matrix is well known. The reaction temperature is controlled by an electrically heated oven and the sample thermo-couple was placed marginally above the catalyst. A detailed description of the apparatus has been described previously [9].

2.3. *Catalysts*

Copper foil (Aldrich, thickness 1.0 mm, broadness 3.5 mm), copper mesh 40 (Aldrich) and mesh 200 (Aldrich) were used as elemental unsupported catalysts.

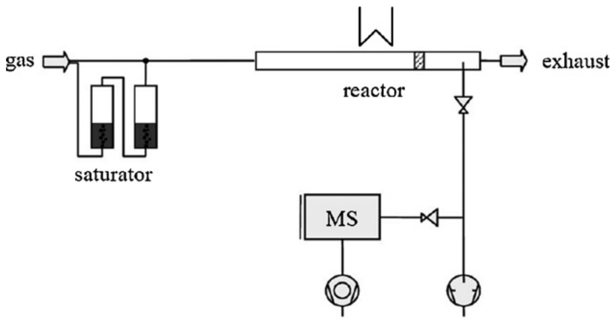

Fig. 2. Scheme of the tubular reactor including the gas unit, the reactor and the analytics.

2.4. *Pre-treatment*

The catalysts were first heated and then stressed by consecutive redox-cycles until steady state conditions with regard to the relative mass change (TG-signal) and activity (DTA-signal), were reached. Each redox-cycle consists of different parts:

(a) oxidation phase: oxygen 6 vol.%, 30 min,
(b) reaction phase: ethanol 6 vol.% + oxygen 3 vol.% or hydrogen 4 vol.% + oxygen 2 vol.%, 90 min and
(c) reduction-phase: ethanol 6 vol.% or hydrogen 4 vol.%, 15 min.

2.5. *CP-reaction*

Concentration programmed reactions were performed where the concentration of the reductant (ethanol 6 vol.% or hydrogen 4 vol.%) was held constant and the concentration of oxygen was changed stepwise. The size of each oxygen step was 1 vol.%. Starting with 6 vol.% (in the case of ethanol) or 5 vol.% (in the case of hydrogen) the concentration of oxygen was changed stepwise to 0 and back again to 6 or 5 vol.%, respectively. Before performing the next O_2-step the response of the system was followed till the system remains at steady state for at least 1 h. The volumetric flow rates remained constant during CP-experiments and the total volume flow was 100 ml min^{-1} (standard conditions).

3. Results

3.1. *Pre-treatment*

One of the challenges in Cu-catalysis is the length of time it takes for the reaction system to achieve steady state. Depending on the respective chosen conditions a strong restructuring process of not only the surface but also the bulk occurs [10]. This is the reason why the fresh catalysts were pre-treated by consecutive redox-cycles. To assess the pre-treatment the TG- and DTA-signals were used as indicators.

In Fig. 3 the relative mass changes of the catalyst at the end of each oxidation phase and the activities of the catalyst at the end of each reaction phase are shown for the consecutive performed cycles ($T = 360\,^{\circ}$C, mesh 40, 7.5 mg). During the pre-treatment the catalyst activity (DTA-signal) only rises slightly from 69 to 76 μV, whereas the mass change (TG-signal) exhibits a maximum in the third cycle. In the first cycle the fresh copper (see Fig. 4a) consists of single copper particles with a relatively smooth surface.

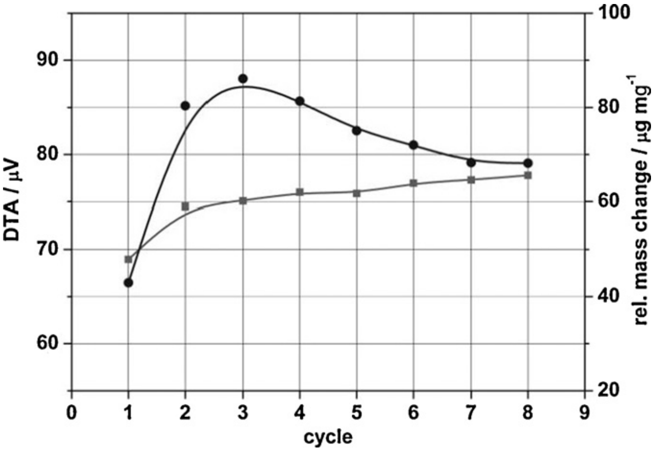

Fig. 3. DTA-signal (■) and relative mass change (●) during the alternately applied redox-cycles (6 vol.% $O_2 \rightarrow$ 4 vol.% O_2 + 2 vol.% $H_2 \rightarrow$ 4 vol.% H_2 only) at 360 °C on copper mesh 40.

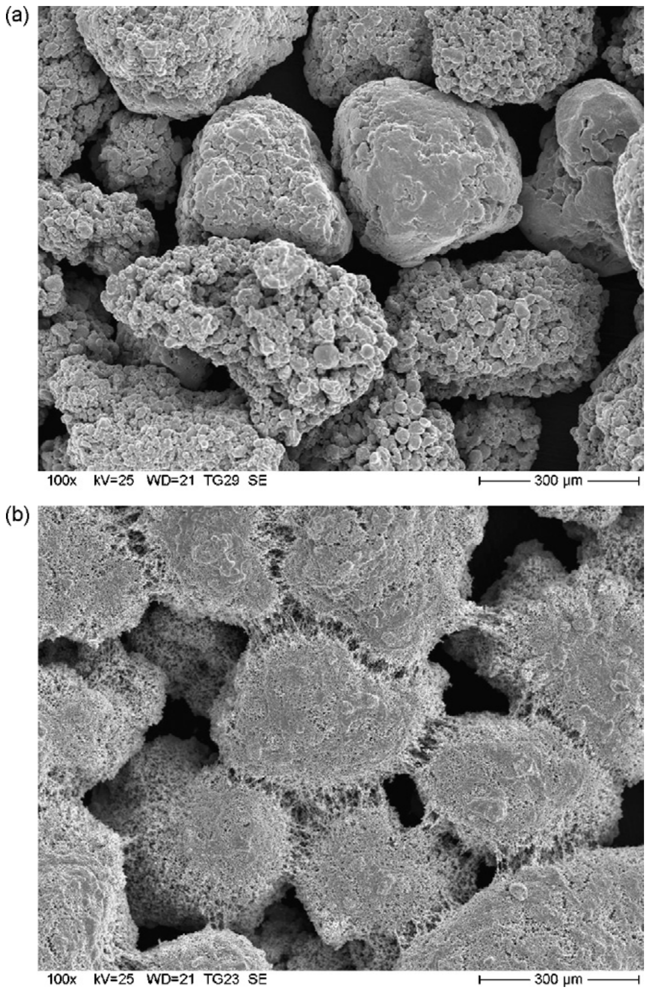

Fig. 4. Scanning electron microscopy (SEM) pictures (25 kV electron beam, secondary electrons detector) of fresh (a) and pre-treated (b, third cycle) copper mesh 40. The SEM images indicate the morphological changes during pre-treatment.

By proceeding the pre-treatment significant changes on the surface morphology occurs which are superposed by a sintering of the copper grains (see Fig. 4 b). Between the copper particles the formation of needle-like structures is observed. During the first cycle strong restructuring and roughening leads to a higher surface and a slightly increased activity. But, due to the superposed sintering the active surface decreases during the following cycles and the measured mass changes exhibit a maximum. Pre-treatment studies were performed on up to 12 redox-cycles but under the chosen conditions 8 redox-cycles were sufficient to achieve a pre-treatment state.

It should be noted that the pre-treatment plays a significant role for the later performance of the Cu-catalyst and is essential in order to obtain reproducible data. If hydrogen is used as the reductant the morphological changes are visible to the naked eye. In the case of ethanol these effects can also be observed but not as significant as in the case of hydrogen.

3.2. CP-reaction

3.2.1. Hydrogen-oxidation (TG/DTA-apparatus)

The oxidation of hydrogen was introduced as the model reaction in order to avoid side reactions and carbonization of the catalyst. During the CP-reactions performed in the TG/DTA-apparatus the catalyst activity can be observed by the DTA-signal. The DTA-signal in dependence of the fed oxygen amount is shown in Fig. 5. For each measuring point the system remained at steady state for at least 1 h. The experiment was started with 5 vol.% O_2 and 4 vol.% H_2. Afterwards the volume fraction of O_2 was reduced stepwise from 5 vol.% to 0 and then increased back again to 5 vol.% (upwards). By decreasing the concentration of oxygen (Fig. 5, lower branch of the hysteresis) the activity of the catalyst exhibits a maximum at 3 vol.% O_2. The catalyst activity shows a linear dependency if the O_2 concentration is decreased below this point. Starting now from lean conditions the DTA-signal continues to show a linear dependency up to 3 vol.% O_2, but compared to the downward changes the catalyst has a significantly higher activity (Fig. 5, upper branch of the hysteresis) at 4 and 5 vol.% O_2. It is obvious that under the chosen condition a hysteresis for the system copper–oxygen–hydrogen can be seen clearly. A further increasing of the oxygen concentration above the maximum activity point (4 vol.% $O_2 \rightarrow$ 5 vol.% O_2) leads to a deactivation of the catalyst and the hysteresis gradually closes.

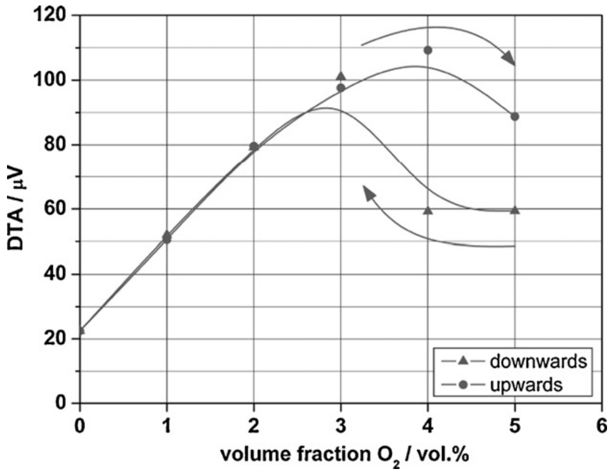

Fig. 5. A hysteresis loop of the DTA-signal as a function of the oxygen volume fraction is shown ($H_2 + O_2$ on 7.5 mg copper mesh 40 at 360 °C). The volume fraction of O_2 was decreased stepwise from 5 to 0 vol.% and then increased again to 5 vol.%.

It is well known that the activity and selectivity of the copper catalyst depend strongly on the oxidation state of the surface and subsurface [5–7,11]. Furthermore the oxygen-to-reductant ratio in the feed stream affects the oxidation state of these regions. The pure metal is not an active catalyst, whereas completely oxidized copper is unselective and favors the combustion. The hysteresis with its higher activities of the catalysts in the upper branch (Fig. 5, 4 and 5 vol.% O_2) could be explained by the TG-signal, whereas our method is not able to distinguish between surface, subsurface and bulk phase. Comparing the catalyst mass changes at 4 vol. % O_2 for the upper (TG-signal: 900 µg) and the lower branch of the hysteresis (TG-signal: 1320 µg) indicates that copper in the higher oxidation state is less active than copper in a middle oxidation state. Species in a middle oxidation state would also explain the reduction kinetic of the catalyst during the CP-reaction (see Fig. 6). Here, the catalyst was run under slightly oxygen-rich conditions (e.g. 4 vol.% H_2 and 4 vol.% O_2) at steady state. Then the oxygen was switched to 3 vol.% O_2. Remarkable is that although the amount of oxygen was decreased, the activity of the catalyst increases and the temporal acceleration of the activity gives a hint for an autocatalytic reaction. At the same time the catalyst mass changes complementary. So, this autocatalytic behaviour is an evidence for the existence of a middle oxidation state with a high activity.

Furthermore, the broadness and the position of the hysteresis are influenced by the concentration of the reductant (Fig. 7) as well as the temperature (Fig. 8). The hysteresis loop narrows and shifts towards lower volume fractions of oxygen if the con-

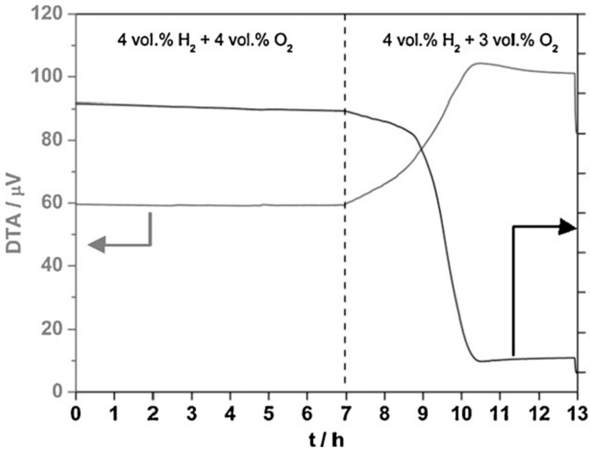

Fig. 6. DTA-signal and TG-signal during a reduction section of copper mesh 40 at 360 °C. In the course of the reduction this process accelerates itself which indicates an autocatalysis.

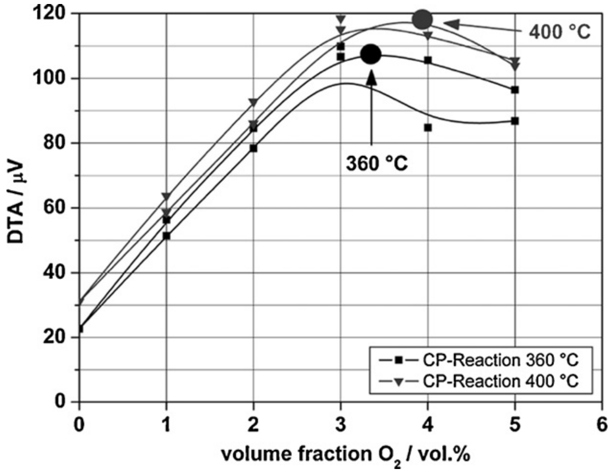

Fig. 8. Comparison of catalyst activity (copper mesh 200, 7.5 mg) as a function of the oxygen volume fraction and at different temperatures.

centration of H_2 is decreased (Fig. 7) or higher volume fractions of oxygen if the temperature is increased (Fig. 8). By increasing the temperature the maximum for the activity shifts to higher oxygen concentrations.

Due to the long reaction time (up to 150 h) and the chosen conditions the copper catalyst undergoes strong changes in structure. Mainly if hydrogen was used as the reductant the changes in structure are significant and after the experiments the catalyst was destroyed totally. The hydrogen diffuses into the copper lattice and reacts with bulk oxygen to water. The water leaks from the copper along grain boundaries and holes in the copper structure result. This is known as pinholing [12]. The first experiments were started with copper mesh 40 but during the course of the investigations it was observed that the length of the reaction times could be shortened and the reproducibility could be improved by using a catalyst with a smaller grain size. For this reason we used copper mesh 200 as the catalyst.

3.2.2. Ethanol-oxidation (U-tube reactor)

In order to obtain more information about the catalyst's selectivity the oxidation of ethanol was introduced as model reaction. In this case both the selective oxidation to acetaldehyde and the combustion take place. Contrary to the oxidation of hydrogen the dynamics of the catalytic system are more complex during the oxidation of ethanol. For example in Fig. 9 the outlet concentrations are shown for a CP-reaction of ethanol on a copper foil at 360 °C. Here, only a small section of the whole experiment is shown where the molar ratio of ethanol to oxygen is 1:1. The dynamics of the Cu-catalyst are remarkable. Although the reaction parameters (T, p and c_{inlet}) are constant the catalyst switches autonomously between two different active states with different overall selectivities. During periods where the partial oxidation takes place oscillations are no longer observed. Oscillations can be reproducibly observed at high oxygen concentrations (5 and 6 vol.% O_2) and in a temperature range between 360 and 440 °C but only in connection with a favored combustion. The oscillations periods are in the range of 30 s. At first the system oscillated with small amplitudes and during the reaction these became larger. The value of the amplitudes reaches a maximum 1% of the volume fraction. Taking a closer look at the oscillations (Fig. 10) the acetaldehyde oscillates with noticeably smaller amplitudes than the combustion products. This observation points out the existence and the presence of different selective oxygen species for partial oxidation and combustion. Such species were also reported in the scope of the oxidation of methanol to formaldehyde [2].

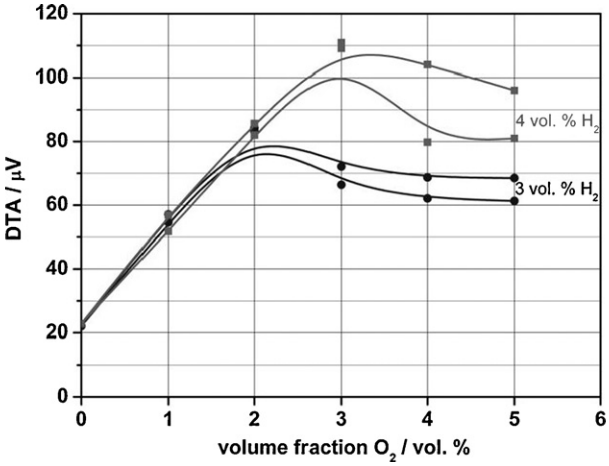

Fig. 7. Comparison of catalyst activity (copper mesh 200, 7.5 mg) as a function of the oxygen volume fraction and at different hydrogen concentrations.

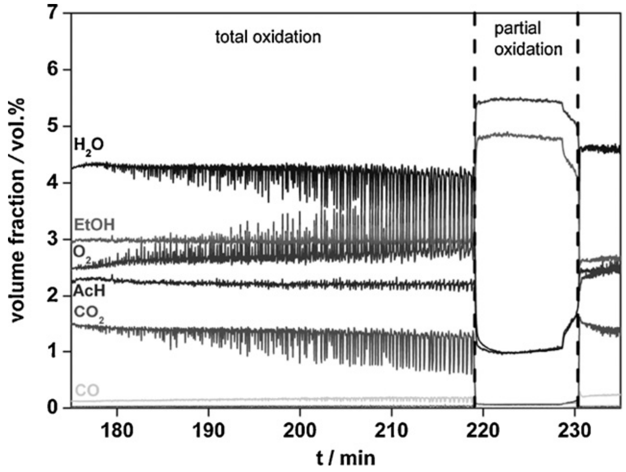

Fig. 9. Volume fraction as a function of time for the CP-reaction of ethanol at 360 °C on 12.5 mg of pre-treated copper foil. The vertical dashed lines indicate the switch of the catalyst between partial and total oxidation, although the feed concentration has not been changed. The molar ratio of ethanol to oxygen is 1:1.

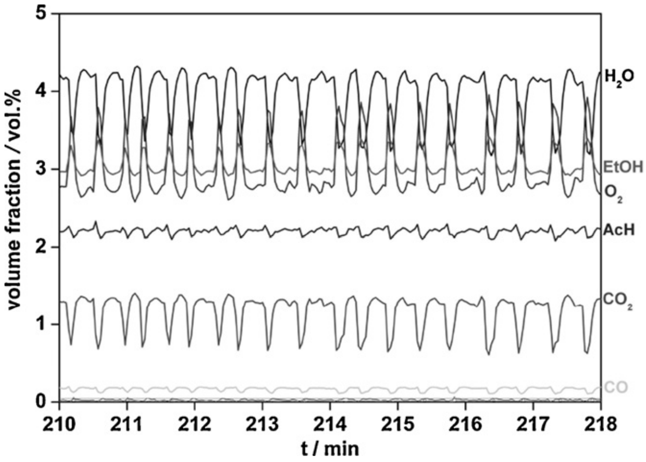

Fig. 10. MS data during an oscillation period for the partial oxidation of ethanol on copper foil (12.5 mg) at 360 °C. The molar ratio of ethanol to oxygen is 1:1.

4. Conclusions

The TG/DTA-apparatus which was used in this work as a reactor is a helpful tool enabling simultaneously the measurement of the activity and the grade of oxidation of the copper catalyst under in situ conditions. Compared to results from the tubular reactor set-up more information is achievable from the pre-treatment state. At this point it should be emphasized that an adequate pre-treatment of the copper catalyst is essential in order to gain a reproducible starting point for later kinetic investigations.

Hysteresis and oscillations are observable under lean conditions, approximately from a stochiometric ratio between oxygen and reductant. In this work the oxidations of hydrogen and ethanol were introduced as model reactions, but such kinetic phenomena were also previously observed in the oxidation of propylene [7] and methanol [4,8]. Their occurrence seems to be independent of the reductant as a result of the intrinsic properties of the copper–oxygen-system. However, it could also be observed that the ranges of these phenomena individually depend on the chosen reductant.

The hysteresis indicates also that it matters if an oxidation on copper is started from lean or rich conditions. In order to gain high activities and selectivities the reaction history plays an important role. Starting from low oxygen-reductant-ratios was the most effective way in this work. Furthermore the temperature proves to be an important parameter for the copper catalysis, because for a given reductant concentration the value of the oxygen concentration where the hysteresis exhibits increases with higher temperatures. Therefore, with increasing temperature the catalyst can be exposed to higher partial pressures of oxygen without oxidizing itself and accordingly without losing its activity or becoming unselective. Summing up, the results of the CP-reaction experiments performed with hydrogen show that the temperature and the reaction history are two important things for the generation and the maintenance of an active Cu-catalyst. Such backgrounds should be noted when running an industrial scale reactor.

Under certain reaction conditions a non-steady state behavior of the catalytic system can be observed although the feed remains at steady state. The observed product distribution during the oscillation phases gives some hints for the mechanism when ethanol is introduced as the reductant. While the rate of the combustion oscillates the rate of the selective oxidation (here: acetaldehyde) remains nearly constant. Most likely there are at least two different sites at the catalyst with different selectivities. In this frame interesting results were obtained by Schlögl et al. during investigations on the oxidation of methanol. Besides oscillations they observed oxygen species on the copper catalyst differing from the well-known pure oxides (CuO and Cu_2O). A middle oxidation state was connected to a high activity and different sites on the catalyst were postulated as an explanation of the selective oxidation and the combustion pathways [5].

Accordingly, the temporary accelerated reaction rate in the CP-reactions (with H_2) when reducing the oxygen concentration to round about the stochiometric ratio (see Fig. 6) can only be explained by the existence of different oxidation states of the copper. At least three different species must be involved for an explanation of such CP-reaction profiles. Based on the known oxides the following reactions would be sufficient to describe an autocatalytic reduction behavior:

$$2CuO + H_2 \rightarrow Cu_2O + H_2O \qquad (3)$$

$$Cu_2O + H_2 \rightarrow 2Cu + H_2O \qquad (4)$$

$$Cu + CuO \rightarrow Cu_2O \qquad (5)$$

Running under oxygen-rich conditions the catalysts remains predominantly in a high oxidation state with less activity. At a certain oxygen-reductant-ratio a middle oxidation state with high activity and consecutively a reduced state with no or less activity are formed. Up to this point everything sounds trivial but it does not explain the temporary accelerated reduction rate. A disproportion where a species of reduced state (CuO) and a species of high oxidation state (Cu^{2+}) react to a species of middle oxidation state might play a key role in this reaction system. This would lead intermediary to an increased rate of the formation of a species of middle oxidation state and due to its high activity to an increased rate of the reduction of the catalyst. So, both the reduction of the high active species in a middle oxidation state and a disproportion would explain the observed autocatalytic like CP-reaction profile.

In this scheme the pure oxides were used for simplicity. It should be emphasised that these drawings can also be done when three other species (in three different oxidation states) participate. So, there is no contradiction to the existence of, e.g. sub-oxide species.

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