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Reaction pathways in methanol oxidation: kinetic oscillations in the copper / oxygen system

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Polycrystalline copper was used as catalyst for the selective oxidation of methanol under stoichiometric reaction conditions for oxidehydrogenation. Temperature-programmed reaction spectroscopy (TPRS) revealed a broad temperature range of reactivity with two distinct maxima for the production of formaldehyde. Phase analysis with thermogravimetry (TG) and powder X-ray diffraction (XRD) under in situ conditions showed that a phase change occurred between the two maxima for formaldehyde production from bulk Cu_2O to metallic copper. Strongly adsorbed methoxy and formate were detected by X-ray photoelectron spectroscopy (XPS) after prolonged catalytic use. A sub-surface oxygen species and surface OH were identified by XPS. A region of oscillatory behaviour was found in the temperature interval between 623 and 710 K. Multicomponent gas analysis of the reaction products with an ion–molecule reaction mass spectrometer (IMR-MS) allowed to derive a reaction sequence in which both methoxy and formate are necessary as surface species. The most selective state of the catalyst for oxidehydrogenation is the co-adsorption system methanol–oxygen. Oxidation of the surface by excess molecular oxygen leads to total oxidation. The catalyst is finally reduced by excess methanol into an inactive pure metallic form. Sub-surface oxygen segregates to the surface and initiates the activity again by enhancing the sticking coefficient for gas phase species.

Keywords: methanol oxidation, methoxy, formate, oscillations, copper oxide reduction, in situ phase analysis, surface analysis

1. Introduction

Methanol oxidation to formaldehyde over copper is an efficient process [1] and has attracted significant scientific interest [2] as model reaction for selective oxidation [3] and with respect to methanol synthesis [4]. A reaction mechanism has been devised with surface science techniques [5,2,6,7] involving methoxy and eventually also formate species. Controversial recent experiments [8,9] concluded that the actual reaction pathway may depend sensitively on the reaction conditions. In these studies of copper surfaces pre-dosed with oxygen [3] and exposed to Langmuir amounts of methanol, strong kinetic effects were noted on the spectroscopic properties of the adsorbates.

The observation of a reaction experiment under technical conditions gives only little information about the microkinetic details or the "reaction mechanism" as a complex convolution of elementary steps results in a superposition of responses of the catalyst mass to the gas phase composition. This was stated in all the recent contributions to the subject highlighting the multiple reaction pathways in this "simple system".

Rate oscillations [10,11] disclose the convolution of individual reactions on the time scale of the oscillation period. Such oscillations in the copper–oxygen system with organic molecules have been described before [12] and were studied in the framework of a phase transition between copper oxides allowing for the action of lattice oxygen as selective oxidation agent. The coupling mechanism was recognised as thermochemical with significant changes of the catalyst temperature controlling rate and selectivity on a time scale of many minutes.

In the present experiments a different type of oscillations with characteristic frequencies of few minutes, drastic temperature changes but also drastic variations in the gas phase compositions were observed for methanol as substrate. The analysis of these oscillations was made possible by the IMR-MS mass spectroscopic detection technique [13,14] allowing the simultaneous quantitative detection of methanol, formaldehyde, formic acid, formic acid methyl ether, methane, hydrogen, carbon monoxide, carbon dioxide and water with a time resolution of 1 s for the sum of all components.

The temporal analysis of the product distribution can be used to answer the question about the relevance of formate and/or methoxy for the main reaction pathways under high pressure flow conditions. The question about the chemical nature of the catalyst under reaction conditions has also to be addressed in order to find the underlying reason for the periodic modulation of the reaction pathway. In particular, the relevance of copper oxides and phase transitions between them is of significance in the light of previous work [15,3,12].

2. Experimental

A copper (111) single crystal, copper foil (0.25 mm thick, 10 × 10 mm), and copper powder prepared by in situ reduction of copper oxide (Fluka, 50 mesh, Cu_2O) were used as catalysts. Methanol to oxygen molar ratios of 1 : 1 were applied without addition of extra water. Nitrogen gas was used to maintain typical space velocities of 1.2–20 min^{-1} in several reactors holding chips of the foil or powder with a total of ca. 1.5 g. Besides several plug flow reactors also a coil of copper tubing served as reactor. Glass and stainless steel, after prolonged use, gave no background reaction. The copper tubing was, however, an active catalyst allowing 22% conversion at 710 K. In the plug flow reactors conversions were achieved of 35% up to 710 K. Temperatures were measured with methane-passivated thermocouples (significant total oxidation on bare thermocouples) spot-welded to a copper chip in the bed. The shifts in the time axis between the responses from the MS and from the thermocouples were calibrated by a jump reduction of CuO with pure methanol (figure 2).

In situ X-ray diffraction was performed with Cu Kα radiation in Bragg Brentano geometry and with a scintillation counter using samples of Cu_2O powder. Scan times were chosen to be typically 2 h with waiting intervals of 2 h after each parameter variation.

XPS data were obtained ex situ with Cu chips after 260 h use in a plug flow reactor. In situ reference experiments with an oxygen pre-dosed single crystal and methanol dosing at 10^{-4} mbar gave qualitatively the same results as with a fresh chip from the Cu foil. An EA 200 MCD analyser operating at 1.0 eV resolution and 300 W of Mg Kα radiation were used. UPS data ensured the absence of charging and gave the calibration of the binding energy scale.

TG experiments under reaction conditions with on-line product monitoring were performed on a Seiko system coupled to the gas dosing and detection system of the plug flow reactors. An Atomica IMR-MS 1500 instrument with Kr/Xe excitation of the mass spectra was used as universal detector.

The TPRS experiments were carried out in quartz tube with an IR-light external heater and a high-speed computer control of the linear heating rate of 5 K/s. Dosing pressures between UHV and atmospheric pressure were possible. A differentially pumped Hiden triple pass mass spectrometer served as sensitive detector.

3. Results

3.1. Phase analysis

In atmospheres of stoichiometric mixtures methanol/oxygen (1 : 1) only Cu_2O was stable above 450 K irrespective of the oxide phase present at 300 K. A typical in situ reduction experiment is shown in figure 1. The starting material was phase-pure Cu_2O as can be seen from the 300 K trace. Between 700 and 800 K the reduction to copper metal occurred with a significant amount of oxide co-existing with the metal within the time window of 4 h under these reducing conditions. The transition temperature was found to depend on the methanol/oxygen ratio with a minimum of 400 K for pure methanol and a maximum of 950 K for pure oxygen. The temperature window in which co-existence of phases occurred was found to depend on the prehistory of the sample. When oxides were reduced with pure methanol the window was very small whereas the window was widened up to 150 K when oxygen was present already during reduction.

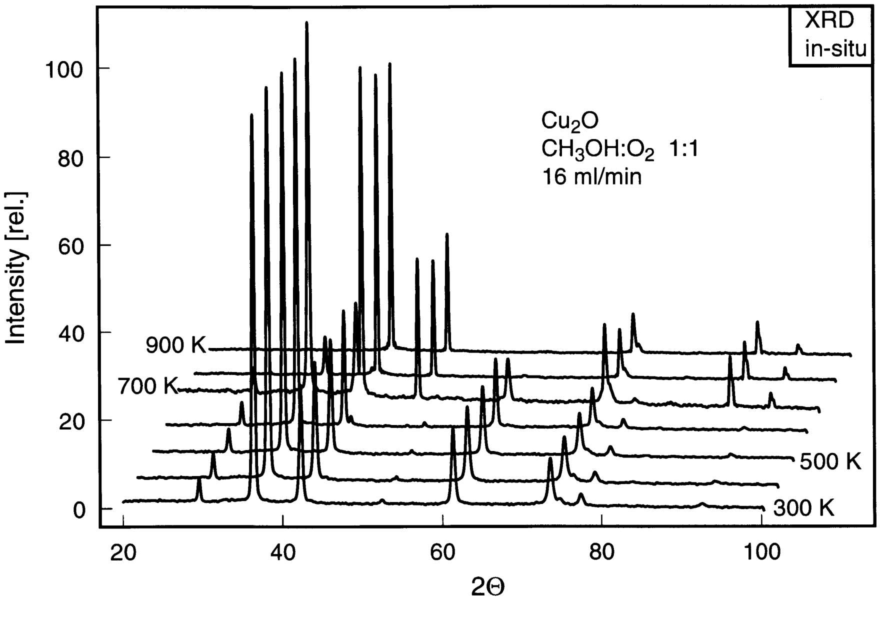

Figure 1. X-ray diffraction wide scans (no internal standard) of a sample of Cu_2O treated in situ with methanol/oxygen. 40 mg oxide were used in a chamber of about 1 ℓ gas volume.

These data were confirmed in the in situ TG experiments shown in figure 2. The weight change was in agreement with a complete conversion from oxide to metal. The reduction kinetics were different for the two oxides with a sharp transition for CuO and a strongly inhibited reaction for Cu_2O. A mixture of oxygen containing copper phases [15,16] was found in a temperature interval of 150 K above 585 K, which is in agreement with the XRD observation. The difference in reduction temperature between the data of figures 1 and 2 was traced back to different heating rates and methanol-to-oxide ratios in both experiments. The inset in figure 2 revealed by differential thermogravimetry (DTG) that the reaction started with a pre-reduction phase at 400 K at which temperature the first metal nuclei will be present at the outer surface of the oxide grains.

Under reaction conditions three ranges of temperatures with characteristic phase compositions were identified. Between 400 and 585 K oxide particles with supported copper metal particles were present. At 600 K these metal particles became detectable by X-ray diffraction (figure 1). Up to about 700 K a transition from oxide to bulk metal occurred. As sub-oxides which should be present in this transition did not give rise to extra lines in the X-ray diffraction analysis [15], their existence may be inferred indirectly as origin for the inhibited reduction kinetics. Above 700 K only copper metal was found irrespective of the high temperature and of the presence of gas phase oxygen.

3.2. Catalytic activity

The three ranges of phase mixtures seemed also to exist on surfaces pre-dosed with oxygen when heated in methanol vapour. Figure 3 reports a TPRS experiment exhibiting two maxima in activity of selective oxidation and an intermediate maximum for the total oxidation activity. The formation of formaldehyde via oxidehydrogenation begins at 400 K and reaches a first maximum at 550 K. A second maximum of dehydrogenation activity was seen above the existence limit of copper oxide phases. The selectivity between total oxidation and partial oxidation was different in the two regimes as seen from the mass 44 trace in figure 3. A maximum in the total oxidation selectivity was observed at temperatures where the bulk observations (figures 1 and 2) indicated the gradual interconversion of oxide and metal.

The two lines in figure 3 denote the temperature range in which oscillatory behaviour was found. Attempts to observe oscillations at pressures below 10^{-2} mbar were unsuccessful in a wide range of parameters. Space velocities at atmospheric pressures of 1.2 to 120 min^{-1} allowed the observation of oscillations.

Typical data taken from the high-temperature end of the oscillatory regime are shown in figure 4. The IMR-MS raw data indicated a conversion of 22.3% methanol. The oscillation amplitude was found to react sensitively to the mean temperature. The amplitude for the formaldehyde production was with 2.6% of the conversion at

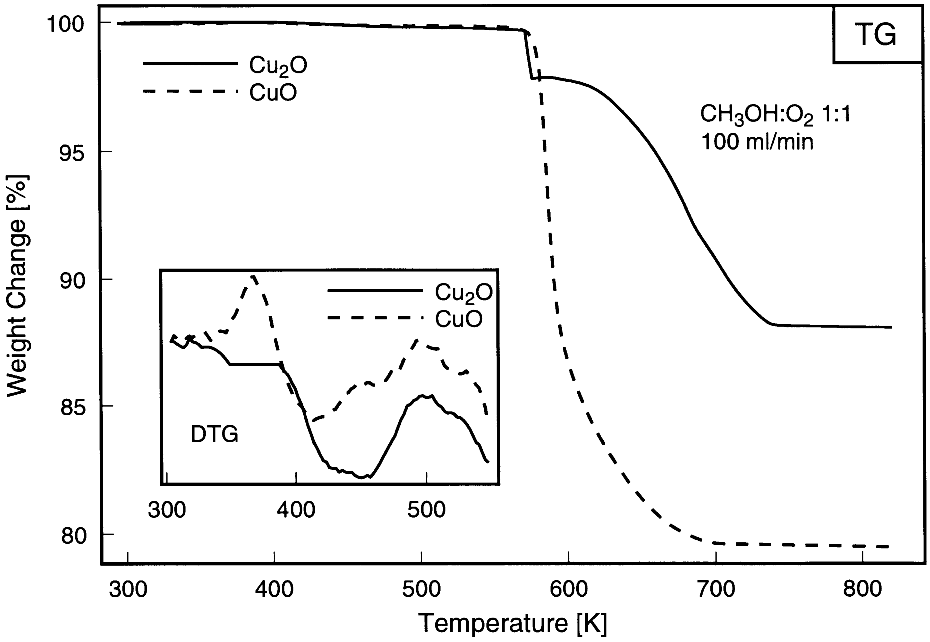

Figure 2. Controlled-atmosphere thermogravimetry of copper oxides in flowing methanol/oxygen. The inset (derivatives of the weight loss curves) reveals small weight changes on a 0.1% scale in the low-temperature region preceding the main reactions. The pre-reactions crate metallic copper at the surface/interfaces of the oxide grains. TG-MS coupling data revealed the initiation of the reaction with methanol at 360 K for CuO and at 410 K for Cu_2O.

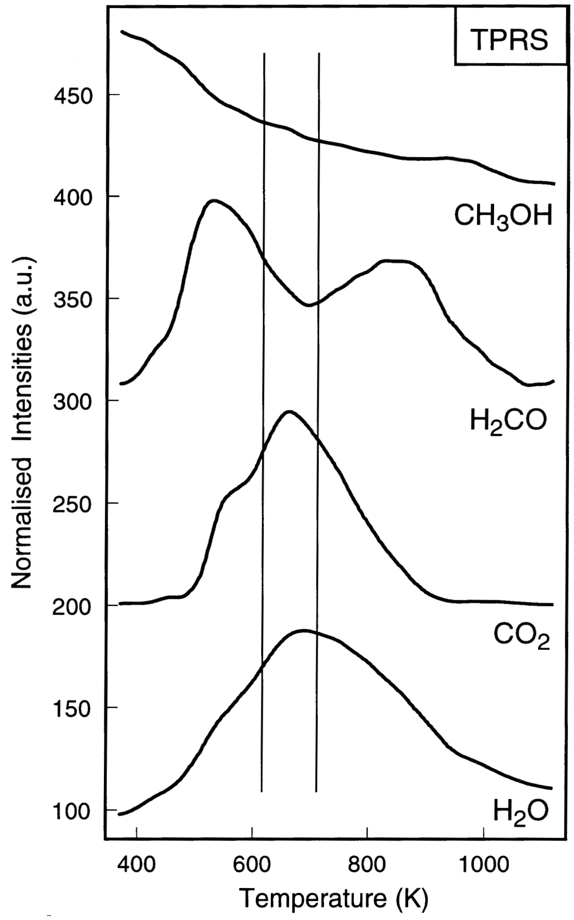

Figure 3. Temperature-programmed reaction spectrum (5 K/min) of a Cu foil pre-dosed with oxygen at 5 mbar for 5 min at 300 K. A methanol partial pressure of 0.01 mbar was applied in a constant volume of 180 ml of a quartz reactor. The vertical lines denote the temperature window for oscillations in the formaldehyde production. The varying ratio of oxygen to methanol in this closed-system experiment gave rise to significant variations in the product selectivity for oxidehydrogenation, dehydrogenation and deep oxidation.

the lower end, at 670 K the maximum amplitude was measured with 55% of the conversion. The selectivity to formaldehyde increased with lower temperature and larger amplitudes as can be seen from the extra area above the horizontal line in figure 4. The reaction pathway of formaldehyde was clearly the oxidehydrogenation route with the product water as followed from the data in the inset of figure 4. An additional reaction to water seemed to inhibit the formaldehyde production as the extra water was always found at the declining side of the formaldehyde peak.

The reaction behaviour was more complex at 670 K as can be seen from figure 5. At this temperature the regime of doubled frequency of the basic oscillations with a characteristic variation of the amplitude was observed. The catalyst temperature dropped within 55 s from the nominal level by 40 K and increased back to its starting level in a sequence of events giving rise to the broadening of the respective signal in figure 5. This was not due to thermal conductivity problems which led to a constant shift between the time axes of the temperature and gas responses which was removed by calibration. Under conditions of low load (space velocity for methanol vapour 1.4 min^{-1}) the resolution was significantly enhanced as can be seen from figure 6. Under the conditions of a controlled maximum temperature the peak shape of the temperature oscillations was very similar to that of the formaldehyde partial pressure indicating that the variation in rate of the exothermic oxidehydrogenation was the origin of the temperature changes.

The oscillatory behaviour was characterised as thermochemical [11], as a change in the temperature restriction from constant maximum temperature to constant heating power affected the oscillation pattern as can be seen in figure 6. The temperature controller of the reactor acted as external restriction, forcing the system under the given chemical conditions into a simple periodic oscillation. The simple periodicity transformed into a complicated time series upon lifting the restriction.

Formaldehyde was produced essentially via the oxidehydrogenation route as deduced from the similarity of the respective partial pressure signals in figure 5. The signal for methanol was not the mirror image of the formaldehyde signal but revealed the operation of additional reaction pathways by its complex shape. These reactions occurred with maximum conversion under the conditions of minimum formaldehyde production. They produced carbon dioxide, hydrogen, formic acid and its methyl ester (not all traces shown). The shape of the conversion minimum before the initiation of the reaction spike was found to depend on the catalyst material with single crystals and foils giving a minimum plateau lasting for up to 40% of the oscillation period whereas powdered catalysts or aged copper chips (after over 250 h time on stream) gave rise to the behaviour shown in figure 5. The production of carbon dioxide in the reaction spike was neither associated with the liberation of water nor with the consumption of gas phase oxygen (data not shown). The sequence of events can be seen in a close-up on one period presented in figure 7. From the initial period of low activity the spike reaction consumed methanol. From 0.5 min to about 2 min the reaction was dominated by the production of formaldehyde and water using gas phase oxygen (data not shown). The methanol decomposition reaction was not completely suppressed. In the final phase the partial pressures of water and carbon dioxide rose as products of total oxidation. This reaction was ascribed to a reduction process of copper oxide leading to a strongly deactivated surface as seen by the decrease in temperature and by the increase in methanol partial pressure.

3.3. *Surface morphology*

Figure 8 summarises morphological observation on copper chips before and after 150 h time on stream.

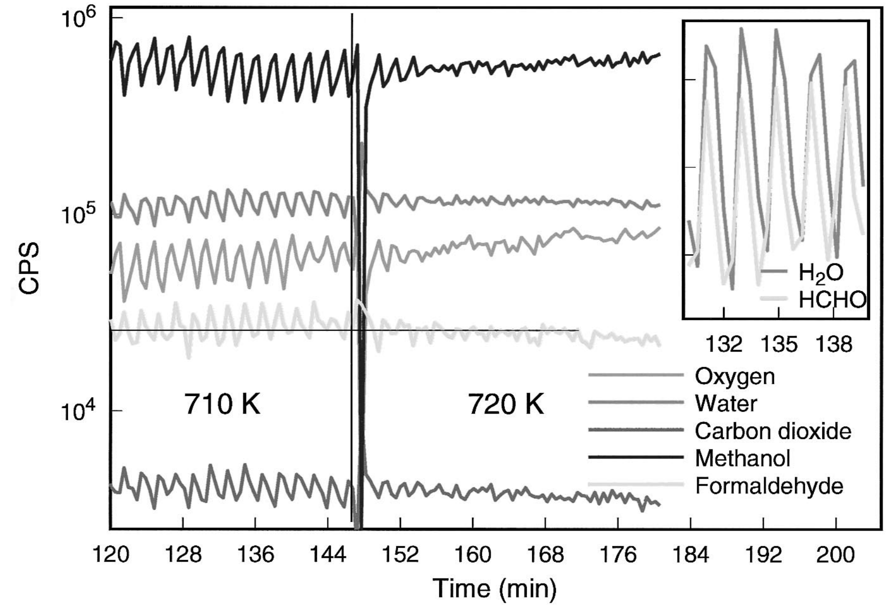

Figure 4. IMR-MS raw data output for an oscillation experiment in a plug flow quartz reactor loaded with copper chips. The sample had seen several days of catalytic testing before this experiment. The vertical line denotes the time at which the temperature controller was changed. The horizontal line in the formaldehyde trace is a guide to the eye to examine the change in yield. The data in the inset were taken from the main panel and suitably normalised.

Images A and B reveal scratches and oxide inclusions (light patches in A) which can be traced back to the manufacturing of the chips. After catalysis (images C and D) the surface was completely restructured. A network of grain boundaries and a smooth hill-and-valley morphology reminiscent on frozen liquids were now the characteristic surface features. Small holes in the formerly closed surface were taken as final confirmation that the reaction not only occurred on the outer surface but also restructured deep volumes underneath the initial metal surface [17].

Occasional non-topographic contrast variations were seen in the low electron secondary electron image. Elemental mapping revealed the presence of

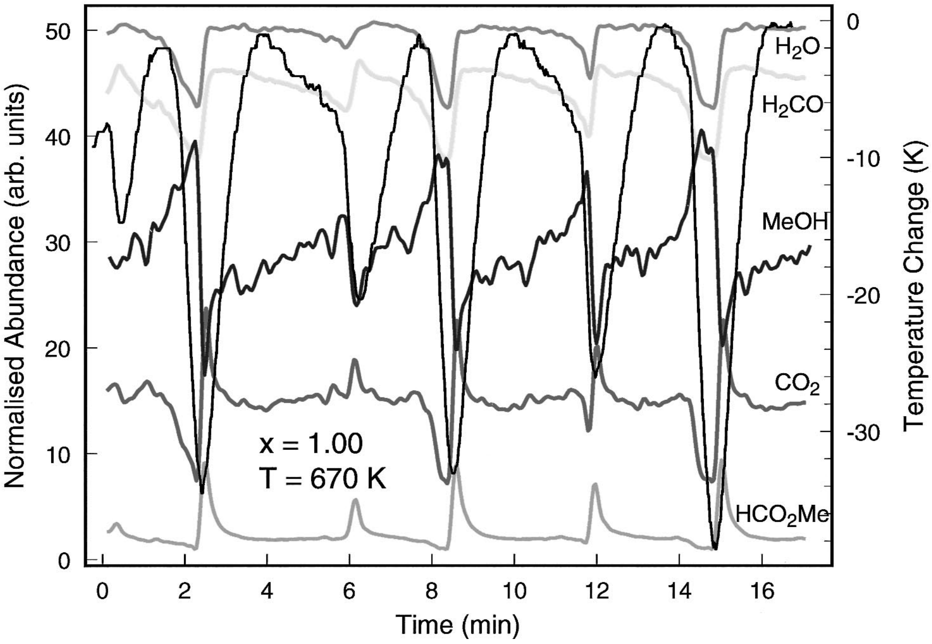

Figure 5. High-resolution scan through an oscillatory episode of the same experiment from which also figure 4 was taken. The data were recorded about 300 min after the data from figure 4. The ordinates are different for the partial pressure traces and the temperature changes. The data are uncorrected for the IMR-MS response functions.

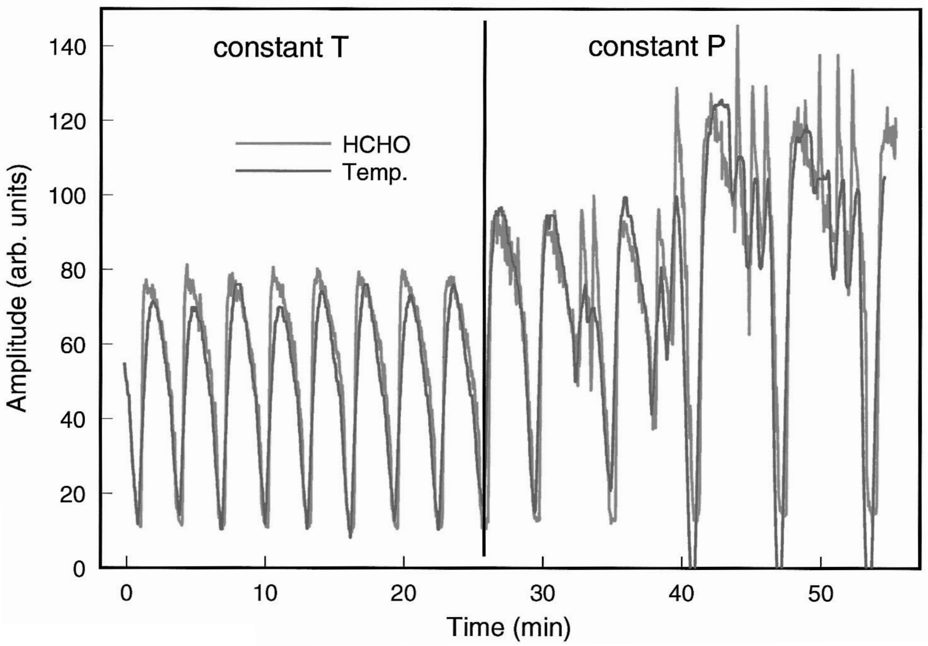

Figure 6. High-resolution oscillation experiment with copper powder ex Cu_2O and at low methanol loading. The residence time of methanol was about 10 s as judged from pulse profile modifications between filled and empty reactor. At the relative time denoted by the vertical line the temperature controller was changed from constant temperature to constant power operation. The set temperature was 670 K. The deviations between the two curves at rapid changes of reactivity give an impression about the thermal inertia of the system giving rise to time delays in the order of 30 s.

oxygen besides that of copper in equal distributions. The patches were thus not due to an oxide particle (which should show up in the element distribution images) but indicated a variation in the surface composition thinner than detectable by 10 keV primary electrons. The presence of oxidic surface patches and the existence of oxygen in sub-surface regions with and without oxide surface coverage [15,18] were found to be characteristic features of all used catalysts.

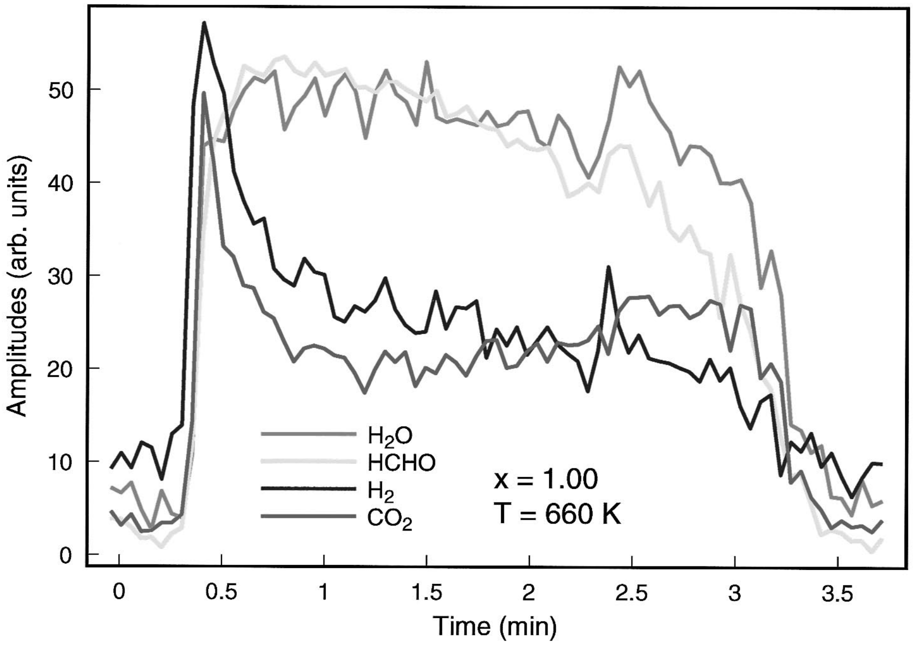

Figure 7. Partial pressure variation during one single oscillation period. Copper chips after 240 h operation under steady state conditions were used. The responses were normalised without correction for the IMR-MS response functions.

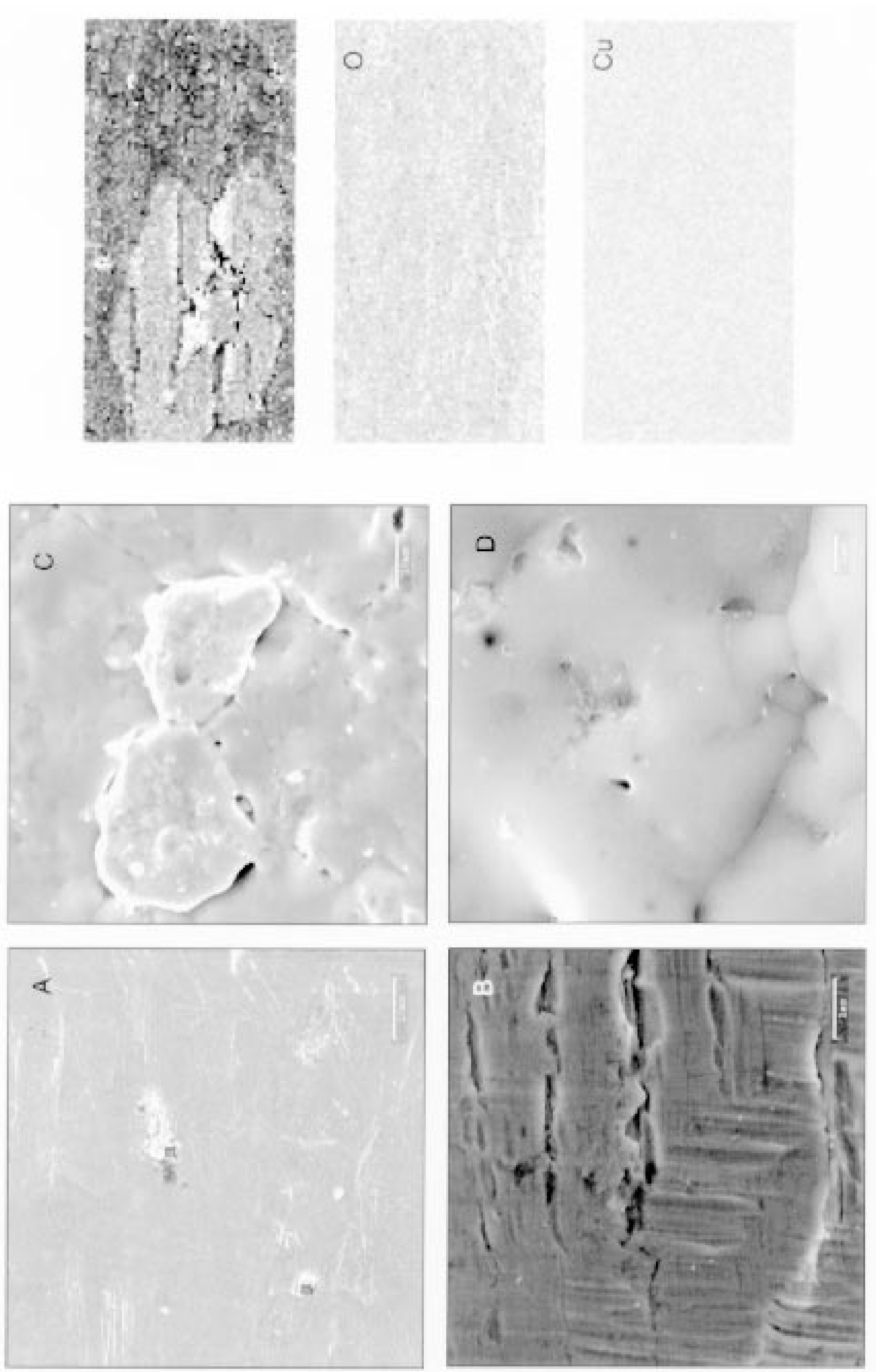

Figure 8. SEM data from copper chips before (A, B) and after (C, D) catalytic testing. The scale bars denote 10 μm (top) and 1 μm (bottom). The acceleration voltage was 30 keV. The three distribution images show the secondary electron yield (top) and the X-ray fluorescence yield for oxygen (centre) and copper (bottom). The acceleration voltage was 10 keV giving rise to comparable sensitivities for the two elements under low absorption conditions.

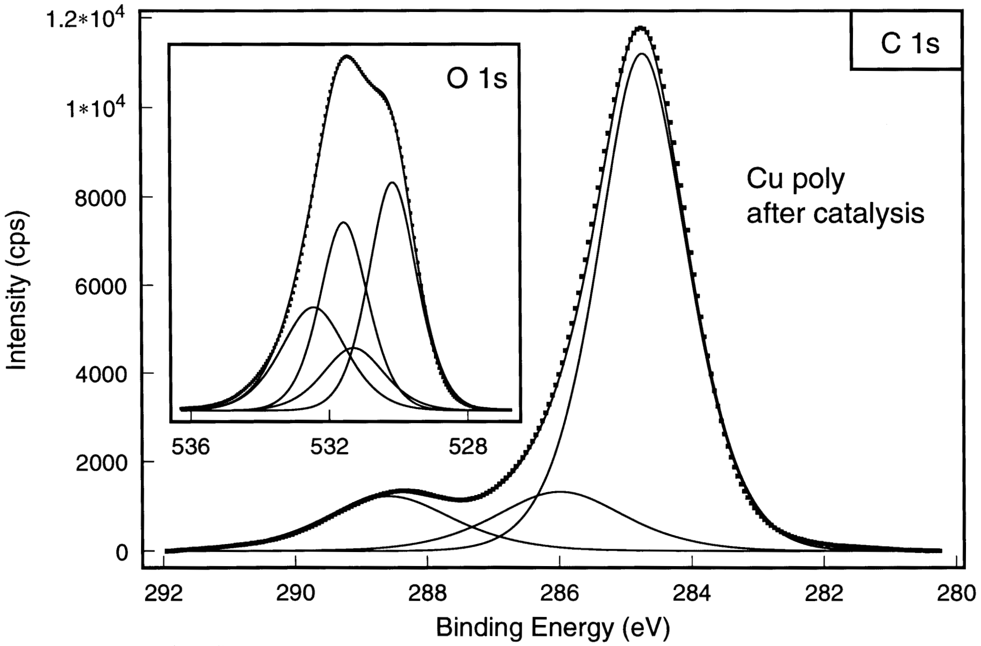

Figure 9. XPS data for C 1s and O 1s of the copper chips after catalytic use (and transfer in air). The peak positions are given in table 2. Several parameters (Gauss–Lorentz ratio, linewidths, positions of the main lines) were taken from reference data of adsorbates on a Cu(111) surface and were kept fixed during the peak fitting procedure. For the assignment see text. The dotted lines represent the experimental data points after satellite and background corrections.

3.4. *Surface analysis*

The presence of oxygen on top and beneath the catalyst surface was investigated with XPS using a Cu(111) single crystal in its clean state and after high pressure oxygen exposure as reference [19] and analysing a chip sample after prolonged time on stream in the reactor. Table 1 summarises the essential results. The copper spectra showed the presence of Cu II species on the surface of the transferred catalyst and on the oxidised single crystal. The oxide layer which may only have formed during isolation of the sample was removed by Ar sputtering leaving a spectrum indistinguishable in main peaks and satellite structures from that of the clean single crystal surface.

Table 1
Selected parameters from surface analysis. All binding energies (BE) in eV

Parameter	Cu(111)	Cu(111) 10 mbar O_2	Cu poly after catalysis	Cu poly Ar-etched
BE Cu $2p_{3/2}$	932.5	932.2 934.3	932.7 934.4	932.6
BE O 1s	–	529.3	530.1 531.6 53.13 [a] 532.4 [b]	530.3 531.6
BE C 1s	–	–	284.7 286.0 [a] 288.5 [b]	285.0
at% Cu	99	52	12	23
at% O	–	48	34	28
at% C	–	–	51	46

[a] Fixed intensity ratio 1 : 1.

[b] Fixed intensity ratio 1 : 2.

The reference sample was free of oxygen after sputtering off the oxide layer. The catalyst sample retained, however, significant amounts of oxygen as dissolved atomic species. A minority contribution of Cu I oxide may have been present, as the Cu 2p spectra of metal and Cu I oxide are difficult to distinguish when the oxide is present as the minority species.

The presence of more than one oxygen species was substantiated by a profile analysis of the O 1s data. In figure 9 the spectra were displayed of the oxygen species and of the strongly abundant carbon adsorbates. The oxygen 1s peak profiles of the two main species were taken from the spectrum of the oxygen adsorbate on the single crystal. The peak at 530.1 eV was ascribed to the Cu I oxide, the line at 531.6 denoted the presence of OH groups from either the transfer or from the catalytic action. Sputtering removed this species whereas the signal at 530.1 eV remained as strong feature. This peak was thus caused also by the oxygen dissolved in the metal [16]. The observation of oxygen by EDX (figure 8) excludes the possible interference of a sputtering artefact.

The two minority species in the oxygen spectrum were required to account for the peak shape. Their existence is further substantiated by the additional lines in the carbon 1s spectrum. The main line of unspecified carbon is accompanied by two carbon–oxygen species with single- (286.0 eV) and double-bonded (288.5 eV) oxygen fully consistent with the presence of methoxy and formate species [5]. With this assignment the peak area ratio (see table 1) of the oxygen species was fixed to account for the correct stoichiometries. These constraints led to a good description of the experimental O 1s profile.

Table 2
Reactions involved in the oscillation sequence for $x = 1.0$

Phase	Reaction
phase 1, short	$\{O\}_{subsurface} \rightarrow \{O\}_a$
phase 2, short	$CH_3OH_g \rightarrow CH_3OH_a$
	$\{O\}_a + CH_3OH_a \rightarrow HCOO_a + 2H_2$
	$2HCOO_a \rightarrow 2CO_2 + H_2$
	$2HCOO_a \rightarrow HCOOH + CO_2$
	$HCOO_a + CH_3OH \rightarrow HCOOCH_3 + H_2O$
phase 3, long	$O_2 \rightarrow 2\{O\}_b$
	$CH_3OH_g \rightarrow CH_3OH_a$
	$CH_3OH_a + \{O\}_b \rightarrow CH_3O_a + OH_a$
	$CH_3O_a + \{O\}_b \rightarrow H_2CO + OH_a$
	$CH_3OH_a + OH_a \rightarrow H_2CO + H_2O$
phase 4, long	$\{O\}_b \rightarrow \{O\}_{subsurface}$
	$2Cu + \{O\}_b \rightarrow Cu_2O$
phase 5, short	$CH_3OH + 3Cu_2O \rightarrow 3Cu + CO_2 + H_2O$

4. Discussion

The combined action of methanol and oxygen on polycrystalline copper at atmospheric pressure and elevated temperatures was not only an efficient surface catalytic reaction but also affected the sub-surface region of the metal by introducing atomic oxygen and by restructuring the surface topography. Thermochemical oscillations were observed as well as the presence of strongly adsorbed reaction intermediates methoxy and formate which all pointed to the combined action of several reaction pathways. The main reaction pathway was the oxidehydrogenation of methanol:

$$2CH_3OH + O_2 \rightarrow 2CH_2O + 2H_2O \quad \Delta H_{670} = -264 \text{ kJ/mol.} \tag{1}$$

Under oscillatory conditions the strongly exothermic formaldehyde production is in competition to the energetically similar oxidation of the copper catalyst:

$$4Cu + O_2 \rightarrow 2Cu_2O \quad \Delta H_{670} = -239.4 \text{ kJ/mol.} \tag{2}$$

The resulting copper oxide is effectively reduced by methanol back to pure metal:

$$CH_3OH + 3Cu_2O \rightarrow 6Cu + CO_2 + 2H_2O \quad \Delta H_{670} = -305 \text{ kJ/mol.} \tag{3}$$

The surface coverage with oxygen will determine the activity of the catalyst which is inactive for zero coverage [5,8,9] and unselective for full coverage. Oxygen can be supplied to the surface through the gas phase or through diffusion from the sub-surface region onto the interface. This is of relevance as after a complete reduction of the surface by methanol (eq. (3)) also the fractional surface coverage with oxygen is missing which is required to enhance the sticking coefficient of gas phase species onto the copper surface.

A reaction scenario describing the oscillations observed can be the following. At zero time of each period (see figure 7) the surface consists of metallic copper and is inactive due to low sticking coefficients [7] of all gas phase species. During the inhibition time (ca. 0.3 min, figure 7) sub-surface oxygen diffuses to the interface. Its presence leads to chemisorption of methanol and to its oxidehydrogenation to formate which rapidly covers the whole surface [9,4]. Hydrogen and now adsorbing methanol lead to desorption of formic acid and its methyl ester (see figure 5) as side reactions besides the most efficient path of formate decomposition to carbon dioxide. The oxygen required for this decomposition stems from the sub-surface reservoir leading to a rapid decrease of the efficiency of this reaction scenario. The main reaction involving the co-adsorption of gas phase oxygen and methanol and its conversion through methoxy to formaldehyde and water wins the competition for the empty sites on the copper surface within ca. 0.2 min (see figures 5 and 7). The increasing temperature caused by the excess energy from reaction (1) destabilises the copper metal–adsorbate system within about 1.5 min (see figures 5, 6 and 7) by allowing adsorbed oxygen to overcome the barrier for substrate oxidation. Surface oxygen is diffusing into the sub-surface layer replenishing the bulk reservoir and assisting the beginning oxidation of the surface into copper I oxide. This decelerates the methanol-to-formaldehyde reaction. The oxide is finally reduced totally to bare metal with the products carbon dioxide and water. Now the cycle of materials is closed for the following oscillation.

The decreasing rate of formaldehyde production leads to surface cooling which is counterbalanced by the heat liberation from reactions (2) and (3) giving rise to the complex pattern of the temperature-vs.-time curve seen in figure 5. The control parameter which decides over surface oxidation vs. surface total reduction is the methanol-to-oxygen ratio [8]. In figure 5 it can be seen that the break-down of all reaction rates is initiated by a steep increase in the methanol partial pressure. At the molar ratio $x = 1.0$ the gas phase remains reducing as total oxidation is oxygen-limited:

$$2CH_3OH + 3O_2 \rightarrow 2CO_2 + 4H_2O \tag{4}$$

The formation of copper oxide consumes all oxygen available for total oxidation and shifts the chemical potential of the gas atmosphere from oxidising at the beginning of the oscillation (no oxide) to reducing at the end of the oscillation (maximum abundance of oxide). The excess reducing potential finally destroys the reactivity by removing all oxygen from the copper. Only because of the sub-surface reservoir of atomic oxygen which is inaccessible to the reducing gas phase in short times can the reaction be switched on again by the formate reaction.

The control mechanism of the whole scenario is assumed to be the temperature following the results from figure 6. A similar result was reached in surface science experiments carried out in a different regime of reaction parameters [7]. It is pointed out, however, that this variable is strongly coupled to the methanol to oxygen stoichiometry in the gas phase [8] which also affects the oscillatory regime.

No information about the spatio-temporal organisation is available yet. The surface morphological observations (see figure 8) and the fact that oxygen cannot diffuse through the voids of a closed-packed copper crystal [15] imply that the grain boundary network providing transport pathways [20] into the bulk may be relevant for the process. The limited amplitude points also to an incomplete synchronisation involving non-surface processes like restructuring and grain movement.

The whole reaction sequence is summarised in table 2. All steps with observable products have been shown to occur under practical reaction conditions. The reaction intermediates formate and methoxy were identified as relevant in literature studies [2,5,8]. They were also shown to exist as stable surface complexes on a used and transferred catalyst surface (figure 9). The stability of these species [9] indicates that they are mere side products and not the direct reaction intermediates which, being of identical chemical composition, may differ in details of the chemical bonding from the stationary surface-resident species. Essential in all surface science studies [21,6,7,] and in the present high-pressure observations is the postulate that chemisorbed oxygen must exist in two forms [22,23] with predominant reactivity for either dehydrogenation (O_a) or oxidation (O_b) (table 2). The XPS data did not give evidence for such a distinction. In the analogous silver–oxygen system a similar insensitivity of the XPS data to the details of the adsorbate chemical bonding [24] was stated by applying XAS as complementary technique revealing clearly the different electronic structure of two oxygen species. The phase transition between copper II oxide and copper I oxide [12] plays no detectable role in the present experiments as shown by the in situ phase identification experiments. The existence of sub-surface and even bulk sub-oxides of copper has been evidenced indirectly [15,20,25, 26,18,27] and plays a decisive role in understanding the oscillatory behaviour. Under stationary reaction conditions this reaction pathway will be the more relevant the larger is the excess of methanol over gas phase oxygen.

In conclusion, the present experiments have shown that both surface intermediates methoxy and formate can co-exist under practical high-pressure reaction conditions on copper. They both contribute to the conversion of methanol. It was not possible to estimate the relative proportion of their involvement under stationary conditions due to the superposition of primary reactions with consecutive reaction steps. It seems plausible that a parallel reaction network is responsible for the finite selectivity to formaldehyde observed on copper under conditions of stoichiometric feeds. The analysis of the oscillatory behaviour has contributed to bridge experimentally the pressure gap between single-crystal experiments and practical reaction conditions.

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